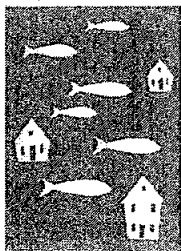


# **EXHIBIT “26”**



*Alewife Neighbors, Inc.*

Cambridge MA 02140

**Alewife  
Neighbors,  
Inc.**

Cambridge, MA 02140

info@

AlewifeNeighbors.org

c/o Michael Nakagawa  
51 Madison Avenue  
Cambridge, MA 02140

23 January, 2004

RTN 3-0277

Tier IC Permit No. 118529

Ida Babroudi  
Department of Environmental Protection  
Bureau of Waste Site Cleanup  
Permit Section at Northeast Regional Office  
One Winter Street  
Boston, MA 02108

by FAX: 617.654.6685

Dear Ms. Babroudi,

Alewife Neighbors, Inc., a 501(c)(3) non-profit organization representing residents in North Cambridge, Massachusetts, would like to thank you for the opportunity to comment on the Tier I permit extension application for the W. R. Grace site at 62 Whittemore Avenue, Cambridge, Massachusetts.

In recent outreach to the neighborhood, two points have become clear: there is still a strong desire to have a public meeting to discuss the W. R. Grace site, and people are uncomfortable with the explanation for the asbestos contamination in the soil. Consequently, we appreciate that Grace is honoring our request to hold a public meeting.

However, we remain concerned that without a full understanding of how such large concentrations of asbestos in the soil could be found scattered through the site, we cannot be certain of the risk of exposing pockets of asbestos during soil-disturbing activities on the site. Recently, we have been made aware of numerous patents involving the use of asbestos that were granted to Grace employees in the Boston area. Activities involving these processes may have occurred on the site but have not been mentioned.

Therefore, we feel justified in requesting that as a condition of renewing the Tier I permit, Grace should be required to give a full disclosure of products and processes developed at the site, so that we can be assured that the asbestos contamination is not the result of site activities, and therefore, that the risk of exposing even higher concentrations of asbestos in the soil at the site is small.

Thank you for considering our request.

Sincerely,

A handwritten signature in dark ink, appearing to read "Michael Nakagawa".

Michael Nakagawa  
Alewife Neighbors, Inc.

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SL = U/A

January 22, 2004

RTN 3-0277 AND 3-17014

62 Whittemore Ave  
Cambridge, MA

Massachusetts Department of Environmental Protection  
Bureau of Waste Site Cleanup  
Permit Section  
Northeast Regional Office  
One Winter Street  
Boston, MA 02108

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JAN 26 2004

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To Whom It May Concern:

NORTHEAST REGIONAL OFFICE

It has come to our recent attention that W.R. Grace & Co. has submitted a Permit Extension Application for the above referenced site at 62 Whittemore Avenue, Cambridge, MA. This application proposes to extend the permit for this site to "18 March 2005".

The rationale for this extension is given as "that additional time may be required to complete and finalize all necessary filings."

Referenced in this letter is the claim by W.R. Grace that MADEP is currently involved in an "Administrative Completeness Review of the Application". Although the referenced purpose of this "review" is limited to the application itself, MCP is a structured process with specific milestones and benchmarks that are both interdependent and necessary.

Because of this structure, it is imperative that all previous requirements be met before proceeding to additional permissions and allowances.

The Alewife Study Group and other concerned citizens have consistently pointed out that the site description and history provided by W.R. Grace's LSP are both materially and literally deficient. Although we are not scientists, we have pointed out in the past that discrepancies have occurred. And we have from time to time provided evidence of such.

Given this history it is once again unfortunate to have to point out that the Phase I requirement of an accurate and forthright description of site history is still as of yet incomplete at best, particularly with respect to asbestos usage.

W.R. Grace has maintained consistently and as recently as November 24, 2003 that site activities involving asbestos were limited to "pilot scale" operations and "small amounts" associated with research and development. On page 35 of the November 24, 2004 *Report On Phase II Comprehensive Site Assessment for the Presence of Asbestos*, W.R. Grace claims that:

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"The demolition of the former buildings, the degradation of the asbestos containing building materials, and releases of fibers from automobile brakes (a friction product) are likely the source of the low levels of asbestos present in the soil".

The idea that automobile braking residue and SACM's are likely sources for the unusually high level of asbestos in deeper subsoils is of course inane. But what is more distressing is that apparently W.R. Grace has not fully disclosed the various formulations including fiber additives of major products which are known and have been disclosed. Moreover, there is no evidence that the LSP has bothered to ask about these major products, which even Grace does not deny that it produced at this site in massive quantities over many decades.

On page 4 of the November 24, 2004 *Report On Phase II Comprehensive Site Assessment for the Presence of Asbestos* it is claimed that:

"The Dewey and Almy facility originally manufactured materials used as can sealing compounds, drum and pail cover gaskets, and bottle cap gaskets."

In fact a wide range of products were produced at this site including soldering fluxes, thermoplastic coatings, soda lime agents, catalysts, dispersing agents, adhesives and grinding aids for portland cement. Since W.R. Grace did manufacture these products at this facility for worldwide consumption, I would have thought that the LSP might have asked for a complete description of all patented formulations involving these known products.

According to the United State Patent Office, the following patents specifying or suggesting asbestos fiber additives to gasket and similar products were granted to W.R. Grace specifically at this location as opposed to the NY office or the Connecticut or other facility as was the general practice:

- **3971785** Assignee: W.R. Grace, Cambridge, MA by Thomas A Messina (Waltham) and Patrick J. Droney (Arlington) - 1975
- **3834578** Assignee: W.R. Grace, Cambridge, MA by David B. Smith (Watertown) and Joel A. Gribens (Framingham) - 1972
- **3365096** Assignee: W.R. Grace, Cambridge, MA by Robert D. Eckert (E. Arlington, MA) - 1966
- **4182649** Assignee: W.R. Grace, Cambridge, MA by Andrew B. Holmstrom and Norman J. Hayes - 1980
- **3555122** Assignee: W.R. Grace, Cambridge, MA by Charles W. Simons (Bedford, MA) - 1966

- **3557030** Assignee: W.R. Grace, Cambridge, MA by Charles W. Simons (Bedford, MA) 1966
- **4081503** Assignee: W.R. Grace, Cambridge, MA by Keith Shotbolt - 1974
- **4119746** Assignee: W.R. Grace, Cambridge, MA by Irving E. Isgur (Framingham) And Andrew Holmstrom (Burlington) and Norma J. Hayes (Bedford) - 1977

This list is by no means comprehensive. It represents only a limited and cursory search. The notion that can and bottle sealants would not contain fiber additive is wholly at variance with established industry practice. Most major gasket producers utilized the same range of filler additives and they most certainly included asbestos.

Given the wide dispersal of loose fiber at significant depth and in the surficial soils as noted by testing conducted by USEPA, this source more fully and credibly explains the presence of asbestos at the site. It is most certainly a part of the larger picture.

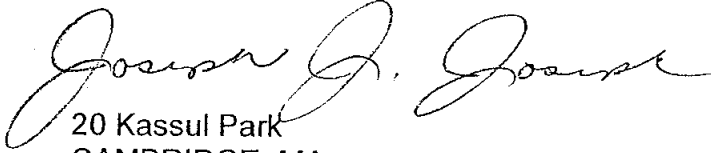
At the very least there ought to be some revision of the historical description of site activities with respect to asbestos usage. Such utilization of asbestos fiber with a major product over many decades indicates the need to account for the use of asbestos in other products manufactured at this facility and most importantly how asbestos waste product was disposed. I would assume that some record of such disposal exists and that it can be provided by the Responsible Party (W.R. Grace) through their LSP (Haley & Aldrich).

Our request for a more detailed description of site activities is, therefore, justified and sufficiently limited. We must however express our dismay that once again the neighborhood has had to challenge the Responsible Party even though there is supposedly a Licensed Site Professional retained and presumably engaged. We do not believe that we should be put in the position of enforcers. And we also believe that this sort of deferral does not comport with the spirit or the letter of MCP. It is even less justifiable given the lack of TAG funding.

We would respectfully recommend therefore that any extension of the Phase II or other permits be reserved until all of the foundations of the prior phases are completed with credibility. This would specifically apply to historical accounts of site activities.

Respectfully Submitted on behalf of the Alewife Study Group

Joseph J. Joseph

A handwritten signature in cursive script, appearing to read "Joseph J. Joseph".

20 Kassul Park  
CAMBRIDGE, MA  
02140

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USPTO PATENT FULL-TEXT AND IMAGE DATABASE

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( 42 of 59 )

**United States Patent****4,182,649****Isgur , et al.****\* January 8, 1980****Polyurethane foam sheet and method****Abstract**

Disclosed herein is a composite, self-supporting, polyurethane foam sheet prepared by forming an aqueous dispersion of hydrophilic polyurethane foam particles with fibers to serve as a binder therefor, wet-layering the dispersion onto a supporting screen to form a sheet, and removing water from the sheet. If desired, a porous web, woven or non-woven, e.g. paper, cloth, etc., can be positioned on the screen with the dispersion being layered out onto the web to form a laminar composite structure. Whether in sheet form or as a laminar structure the product of the invention is formed rapidly and possesses a desirable soft or cushioning feel.

**Inventors:** **Isgur; Irving E.** (Framingham, MA); **Holmstrom; Andrew B.** (Burlington, MA); **Hayes; Norman J.** (Bedford, MA)

**Assignee:** **W. R. Grace & Co.** (Cambridge, MA)

**[\*] Notice:** The portion of the term of this patent subsequent to August 29, 1995 has been disclaimed.

**Appl. No.:** **767994**

**Filed:** **February 11, 1977**

**Current U.S. Class:** 162/101; 162/108; 162/155; 162/168.2; 162/169; 162/183; 428/317.9; 428/327; 428/402; 428/423.5; 428/424.8; 428/425.1; 442/221; 442/370

**Intern'l Class:** D21D 003/00

**Field of Search:** 162/183,101,168 N,169,108,145,155 ;317  
428/264,271,286,371,314,425,240,95,306,311,327,315,402,423,323,904,237,248,318  
427/180 260/2.5 AK

**References Cited [Referenced By]**

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**U.S. Patent Documents**

<u>2887431</u>	May., 1959	Piersol	-	162/169.
<u>3149022</u>	Sep., 1964	Griswold		162/169.
<u>3674621</u>	Jul., 1972	Miyamoto et al.		162/157.
<u>3694301</u>	Sep., 1972	Gruenewald et al.		428/292.

**Foreign Patent Documents**

1284090	Nov., 1968	DE.		
47-24263	May., 1972	JP		162/101.

*Primary Examiner:* Bashore; S. Leon

*Assistant Examiner:* Chin; Peter

*Attorney, Agent or Firm:* McCarter; Lowell H., Parker; C. Edward

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***Parent Case Text***

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This application is a continuation-in-part of Ser. No. 656,674 filed Feb. 9, 1976 and entitled, "Foam Sheet and Method", now U.S. Pat. No. 4,110,508.

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***Claims***

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What is claimed is:

1. A method for preparing a compressible, resilient, homogenous composite sheet having sufficiently low modulus of compression to provide a cushioning effect, said method comprising

(A) forming an aqueous dispersion of fibers,

(B) forming an aqueous dispersion of particles of hydrophilic polyurethane foam prepared by dispersing a prepolymer of a hydrophilic oxyalkylene polyol capped with an isocyanate in water and allowing the isocyanate groups to react essentially simultaneously with the water to form polyurethane particles in-situ, wherein said prepolymer is from about 10 to about 60% by weight, based on total weight of prepolymer and fibers, wherein said polyol has a molecular weight from about 200 to about 20,000 and contains at least 50 mole percent oxyethylene units, wherein the size of the polyurethane particles are not less than about 0.01 inch mesh, and wherein from about 7 to about 50 parts of water is used for every part of prepolymer,

(C) mixing dispersion (A) and (B),

(D) wet-layering the mixed dispersion onto a support, and

(E) removing water from the resulting supported fiber/foam sheet.

2. A method as in claim 1 wherein the fibers are *asbestos*.

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3. A method as in claim 1 wherein cellulosic fibers are employed.
4. A method as in claim 1 wherein latex is added to the mixed dispersions before wet layering.
5. A method as in claim 1 wherein the hydrophilic oxyalkylene polyol contain at least 60 mole percent of oxyethylene units in the backbone.
6. A method as in claim 1 wherein from about 7 to about 50 parts of water is used for every part of isocyanate capped prepolymer.
7. A method for preparing a compressible resilient, homogeneous compsite sheet having sufficiently low modulus of compression to provide a cushioning effect, said method comprising:
  - (A) forming an aqueous dispersion of fibers and particles of hydrophilic polyurethane foam by dispersing into an aqueous fiber dispersion a hydrophilic oxyalkylene polyol capped with an isocyanate whereby said capped polyol reacts essentially simultaneously with the water in said fiber dispersion to form particulate polyurethane foam particles in-situ to produce a fiber/foam dispersion, wherein said capped polyol is from about 10 to about 60% by weight based on total weight of capped polyol and fiber, wherein said polyol has a molecular weight from about 200 to about 20,000, wherein said polyol contains at least about 50 mole percent oxyethylene units, wherein the foam particles size is not less than about 0.01 inch mesh, and wherein from about 7 to about 50 parts of water for every part of capped polyol is employed.
  - (B) wet-layering said fiber/foam dispersion onto a support, and
  - (C) removing water from the resulting supported fiber/foam sheet.
8. A method as in claim 7 wherein the fibers are *asbestos*.
9. A method as in claim 7 wherein cellulosic fibers are employed.
10. A method as in claim 7 wherein latex is added to the dispersion before wet layering.
11. A method as in claim 7 wherein the hydrophilic oxyalkylene polyol contains at least 60 mole percent of oxyalkylene units in the backbone.
12. A method as in claim 7 wherein at least 7 parts of water is used for each part by weight of the combined weight of capped polyol and fiber.
13. In the method for preparing a compressible resilient, homogenous composite sheet by forming an aqueous dispersion containing particulate foam and fibers, wet-layering the fiber/foam dispersion onto a support to form a sheet, and removing water from the resulting supported sheet, the improvement comprising using, in place of shredded foam particles, a particulate dispersion of polyurethane foam prepared by dispersing an isocyanate-capped hydrophilic polyoxyalkylene polyol in water and allowing the isocyanate groups to react essentially simultaneously in-situ with the water to provide the foam particles, wherein said capped polyol is from about 10 to about 60% by weight based on total weight of capped polyol and fibers, wherein said hydrophilic polyoxyalkylene polyol has a molecular weight from about 200 to about 20,00 and contains at least 50 mole percent oxyethylene units,

wherein the size of said foam particles is not less than about 0.01 inch mesh, and wherein from about 7 to about 50 parts of water is used for every part of capped polyol.

14. A method as in claim 13 wherein a separate fiber dispersion and a separate particulate foam dispersion are formed and subsequently combined to form the fiber/foam dispersion.

15. A method as in claim 14 wherein the fibers are *asbestos*.

16. The method as in claim 14 wherein cellulosic fibers are employed.

17. A method as in claim 16 wherein latex is added to the dispersion of cellulosic fibers.

18. A method as in claim 14 wherein the hydrophilic oxyalkylene polyol contains at least 60 mole percent of oxyethylene units in the backbone.

19. A method as in claim 13 wherein the hydrophilic isocyanate-capped prepolymer is dispersed in an aqueous dispersion of fibers to form the fiber/foam dispersion.

20. A method as in claim 19 wherein the fibers are *asbestos*.

21. A method as in claim 19 wherein cellulosic fibers are employed.

22. A method as in claim 19 wherein latex is added to the fiber/foam dispersion before wet-layering.

23. A method as in claim 19 wherein the hydrophilic oxyalkylene polyol contains at least 60 mole percent of oxyethylene units in the backbone.

24. A compressible, resilient, homogenous composite sheet comprising in combination, particles of hydrophilic polyoxyalkylene polyurethane foam and fibers intertwined therewith and binding the particles together to form said sheet, the improvement wherein said foam particles are formed by in-situ foaming by dispersing an isocyanate capped hydrophilic oxyalkylene polyol in an aqueous dispersion of fibers, according to the method of claim 12.

25. A sheet as in claim 24 wherein the fibers are *asbestos*.

26. A sheet as in claim 24 wherein cellulosic fibers are employed.

27. A sheet as in claim 24 wherein latex is employed in combination with the fibers.

28. A sheet as in claim 24 wherein the oxyalkylene polyurethane contains at least 50 mole percent of oxyethylene units in the backbone.

29. A composite laminate comprising in combination, particles of hydrophilic polyoxyalkylene polyurethane foam and fibers intertwined therewith and binding the particles together to form a sheet, and a porous web supporting and adhering to said sheet, the improvement wherein said foam particles are formed by in-situ foaming by dispersing an isocyanate capped hydrophilic oxyalkylene polyol in an aqueous dispersion of fibers according to the method of claim 12.

30. A laminate as in claim 29 wherein the web is a woven fabric.

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31. A laminate as in claim 29 wherein the web is a non-woven material.
32. A laminate as in claim 29 wherein the fibers are *asbestos*.
33. A laminate as in claim 29 wherein the fibers are cellulose.
34. A laminate as in claim 29 wherein latex is employed in combination with the fibers.
35. A laminate as in claim 29 wherein the polyurethane foam particles contain at least 60 mole percent oxyethylene units in the polyoxyalkylene backbone.

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### *Description*

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## BACKGROUND OF THE INVENTION

Numerous attempts have been made to rapidly form foam materials into sheets which are homogeneous while possessing structural strength and also retaining the cushioning effect of the foam. For example, "one-shot" procedures for rapidly building up a sheet of polyurethane foam using spray techniques are well known. For many applications it is desirable to incorporate fibers into the polymer mixture.

In U.S. Pat. No. 4,110,508 referred to above a procedure for incorporating fibers is described. In this application hydrophilic polyurethane prepolymer is foamed and the resulting foam is shredded. Subsequently the shredded foam is dispersed in combination with fibers (e.g. *asbestos* or wood pulp) into water and the resulting aqueous dispersion is wet-layered onto a support which can be a screen or fabric web.

The present invention is an alternate and superior method for preparing the sheets and sheet/fabric laminates described in U.S. Pat. No. 4,110,508, said application being expressly incorporated by reference into the present application to the extent U.S. Pat. No. 4,110,508 describes the urethane prepolymer employed, the method of foaming and shredding the foam to produce hydrophilic particles, the preparation of sheets and laminates and describes these products and their utilities.

The present invention is an improvement over the invention of U.S. Pat. No. 4,110,508 in that the separate steps of foaming and shredding the resulting foam are avoided. By use of the present invention a hydrophilic urethane prepolymer is dispersed in water and foamed simultaneously which results in a simplified process as well as a savings in time. Also it is possible to add the prepolymer directly to an aqueous dispersion of fibers to form a sheet having improved homogeneity. In this instance, sheets having improved tensile strength can be obtained.

## DESCRIPTION OF THE INVENTION

The present invention is a compressible, resilient, homogeneous composite sheet comprising in combination, particles of hydrophilic polyoxyalkylene polyurethane foam and fibers intertwined therewith and binding the foam particles together to form a homogeneous sheet. By homogeneity it is meant that the texture of the sheet is generally uniform in terms of strength and appearance. As an

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indication of compressibility and resiliency it has been found that the indentation range at 25% compression of the sheet was from about 0.5 to about 200. After one minute relaxation the range was from about 0.5 to about 250.

Where *asbestos* fibers are employed the indentation range for sheets of the invention is from about 25 to about 200. For cellulosic fibers the range is from about 0.5 to about 5.3. Sheets of the invention using cellulose fibers also exhibit excellent water absorption and vapor transmission. Water absorption is generally at least 350 weight percent based on the weight of sheets at normal room temperature and humidity, e.g. 40%.

In determining indentation range ASTM D-1564 was employed with a rate of compression equal to 0.1 inch/minute at a temperature of 23.degree. C. and 50% R.H. The samples were not conditioned for any length of time prior to testing.

The compressible composite sheet of the invention is prepared by forming an aqueous dispersion of fibers and particles of hydrophilic polyurethane foam. The particles are formed by dispersing a hydrophilic oxyalkylene polyol capped with an isocyanate in water and allowing the isocyanate groups to react with the water to form a particulate dispersion of polyurethane foam particles. When adding the prepolymer it is desirable to agitate the water. The method of agitation is not critical. For example, a common laboratory mixer can be employed. It has been found that in the resulting dispersion the foam particles have a generally uniform size of less than about 0.08 inch and preferably from about 0.03 inch to about 0.01 inch. In forming the dispersion, a surfactant can be employed. However, it has been found that the foam particle size may be undesirably small, i.e. less than 0.01 inch. To avoid this situation, a different surfactant can be used, or the dispersion can be formed without using a surfactant.

It has been found that the dispersion of fibers and foam particles can be formed in several ways. First an aqueous dispersion of foam particles can be formed as described above. This aqueous dispersion can then be combined with an aqueous dispersion of the fibers using suitable agitation so that the foam particles and fibers are uniformly dispersed. Secondly (and preferably) the isocyanate-capped prepolymer can be added with agitation, directly into a dispersion of fibers. It has been found that by using direct agitation, the resulting sheet is more homogeneous. Also the separate processing step of forming an aqueous dispersion of the prepolymer is eliminated. For these reasons the direct addition procedure is preferable.

The steps of applying the aqueous fiber/foam dispersion to a supporting screen or other surface and removing water from the resulting sheet-like product can be carried out using well-known paper making techniques. For example, for small-scale applications the aqueous fiber/foam dispersion can be placed in a Williams pulp testing apparatus. The dispersion will be positioned on the screen and the water phase will drain through the screen and be removed. Subsequently the resulting sheet can be further dried as desired. For large-scale applications the fiber/foam dispersion can be placed in the headbox of a standard Fordrinier machine and dispersed onto a screen. Using this method the sheet can be rapidly formed in large quantities. The aqueous phase drains from the sheet and subsequently the sheet can be dried further.

The binding fibers employed in the present invention include materials such as *asbestos*, wood pulp or other similar materials dispersible in water. The length or size of the fibers is not critical. Very small fibers, e.g. less than 1/4 inch would not exert adequate binding action and fibers larger than about 1 inch would tend to make dispersion in water and other processing steps difficult. However, use of

surfactants or suitable agitation methods could be employed to extend the range of fibers usable in the invention. Other types of fibers useful include glass fibers, polyester fibers, olefinic fibers and polyamide fibers. It has been found that not all fibers, e.g. polyester fibers are useful in every application, i.e. the homogeneity or structural strength of the sheet may be impaired. For example polyester fibers should not be used as the sole binding fiber. It is necessary to add cellulose, *asbestos* or other types of fibers to increase the binding efficiency of the polyester. The binding efficiency of the fibers can also be increased by using any of the suitable, conventional, binding-type latexes, e.g. SBR, vinyl acetate or acrylic latex.

As well known in the art, another factor tending to increase fiber efficiency in binder applications is "beating" or fibrillation to unravel the ends of individual fibers or packets of fibers. This technique is especially useful with cellulosic fibers. Such fibers can be employed advantageously in the present invention.

As is well known in the art, where a cationic fiber such as *asbestos* is employed an anionic latex will precipitate and be effective. However, where an anionic fiber such as wood pulp is employed, it is necessary to add alum or a similar material to precipitate the latex. Where employed, the latex can be added at any convenient step, e.g. the latex can be added to an aqueous dispersion of fibers prior to adding the prepolymer or foam particles. Alternatively the latex can be added following formation of the fiber/foam dispersion.

In forming the fiber/foam dispersion the amount of prepolymer employed will be from about 10 to 60 weight percent based on the total weight of the prepolymer and fibers, but excluding water. The fibers should be from 90 to 40 weight percent using the same basis. Where a latex is employed the amount of latex should be from about 4 to 10 weight percent based on the total weight of prepolymer, fibers and latex.<sup>sup.1/</sup> Within the above ranges it has been found that increasing the amount of prepolymer increases the "softness" or cushioning effect of the resulting sheet but tends to reduce the tensile strength of the sheet. Increasing the amount of fibers employed tends to increase the strength of the sheet but reduce the cushioning effect. Within the above ranges it may also be possible to increase the strength of the sheet and still retain a high degree of softness by dispersing the prepolymer directly in the aqueous dispersion of fibers according to the second method described above. Given the relatively narrow range of ingredients described, it can be easily determined by a series of test runs whether direct addition of the prepolymer is advantageous in view of the particular fiber and other processing conditions employed.

<sup>sup.1/</sup> Higher amounts of latex can be employed but this results in more "rubbery-like" properties in the finished sheet or inefficient use of the latex polymer.

In another embodiment of the invention the fiber/foam dispersion can be wet-layered onto a porous web such as cloth or a non-woven material. Using the Williams apparatus it is possible to position the fabric over the screen. Suction can be applied to facilitate drainage of the water. It has been found that the foam fiber sheet bonds to the fabric to form a laminar structure. For large-scale applications a Fordrinier machine can be modified to insert fabric over the supporting screen so that the fiber/foam dispersion emptying from the headbox is positioned directly on the fabric in sheet-like form. This procedure results in a relatively fast method of providing a soft backing to fabric. To increase binding of the fiber/foam sheet to the fabric, it is desirable to incorporate a latex into the dispersion as described previously.

In preparing dispersions useful in the present invention (foam dispersion--fiber dispersion--fiber/foam

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dispersion) the amount of water employed is not critical. The water level should be sufficient to permit processing of the dispersions, e.g. if the water level is too low in the foam or fiber dispersions it will be difficult to properly disperse the solid phase and the resulting dispersion will encounter separation problems as well as possess an undesirably high viscosity. Where prepolymer is being dispersed in water (with or without fibers), from 7 to 50 parts of water for every part of prepolymer should be employed. In the finished fiber/foam dispersion at least 7 parts of water should be employed for each part by weight of the combined weight of prepolymer and fiber. In forming dispersions the upper limit on the amount of water employed is not critical with the primary consideration being ease of processing, e.g. because water must be removed from the finished sheet, it is desirable to avoid using more water than necessary in dispersing the materials.

#### Hydrophilic Oxyalkylene Polyurethane Foam

The invention utilizes polyether polyurethanes, i.e. the branch-points of the foam are connected by essentially linear polyoxyalkylene chains. The foam is hydrophilic which means that at least 50 mole percent of the oxyalkylene units (excluding any initiators at branch-points) are oxyethylene units with the balance being oxypropylene, oxybutylene or other oxyalkylene units. Hydrophilic foams are utilized in the present invention to insure that the foam particles can be dispersed in water. To promote dispersion in polyethers where the oxyethylene content approaches 60% or so (e.g. from about 60 to 75 mole percent) it may be desirable to use a surfactant such as those specified earlier.

The hydrophilic foam can be made by any of the common processes such as the "one-shot", prepolymer or quasi-prepolymer processes. After the foam is prepared it can be shredded and used as described in U.S. Pat. No. 4,110,508.

For purposes of the present invention it is preferred to use the prepolymer technique in preparing the hydrophilic foam particles thereby avoiding separate foaming and shredding steps. Suitable prepolymers are prepared by capping a polyoxyalkylene polyol with an excess of polyisocyanate, e.g. toluene diisocyanate. Prior to capping the polyol should have a molecular weight of from about 200 to about 20,000, and preferably from about 600 to about 6,000. The hydroxy functionality of the polyol and the corresponding isocyanate functionality following capping is from 2 to about 8. If foams are formed from prepolymers with an isocyanate functionality of about 2 the resulting foam is essentially linear and does not have as much tensile strength as crosslinked foams. Accordingly, if the isocyanate functionality is about 2 a crosslinker can be employed although the linear non-crosslinked foams are operable in the present invention, i.e. the foam particles can be dispersed in water and layered out to form a sheet. Suitable crosslinkers are well known in the polyurethane art and include by way of example tolylene-2,4,6-triamine, ethylene diamine, diethanolamine, diethylenetriamine, triethylene-tetramine, tetraethylenepentamine, and ethanolamine.

Examples of suitable polyols (to be capped with polyisocyanates) include: (A) essentially linear polyols formed for example by reaction of ethylene oxide with ethylene glycol as an initiator. As discussed above mixtures of ethylene oxide with other alkylene oxides can be employed as long as the mole percent of ethylene oxide is at least 60 percent. Also as stated, it may be desirable to use crosslinkers with these systems in which case the crosslinker can be included in the water into which the prepolymer is dispersed. Where the linear polyethers are mixtures of ethylene oxide with, e.g. propylene oxide, the polymer can be either random or a block copolymer and the terminal units can be either oxyethylene or oxypropylene. A second class of polyol (B) includes those with a hydroxy functionality of 3 or more. Such polyols are commonly formed by reacting alkylene oxides with a polyfunctional initiator such as trimethylolpropane, pentaerythritol, etc. In forming the polyol B, the

alkylene oxide used can be ethylene oxide or mixtures of ethylene oxide with other alkylene oxides as described above. Useful polyols can be further exemplified by (C) linear branched polyfunctional polyols as exemplified in A and B above together with an initiator or crosslinker. A specific example of C is a mixture of polyethylene glycol (m. w. about 1,000) with trimethylolpropane, trimethylolethane or glycerine. This mixture can be subsequently reacted with excess polyisocyanate to provide a prepolymer useful in the invention. Alternatively the linear or branched polyols, (e.g. polyethylene glycol) can be reacted separately with excess polyisocyanate. The initiator, e.g. trimethylolpropane, can also be separately reacted with polyisocyanate. Subsequently the two capped materials can be combined to form the prepolymer.

Suitable polyisocyanates useful in preparing prepolymers include toluene-2,4-diisocyanate, toluene-2,6-diisocyanate, commercial mixtures of toluene-2,4- and 2,6-diisocyanates, ethylene diisocyanate, ethylidene diisocyanate, propylene-1,2-diisocyanate, cyclohexylene-1,2-diisocyanate, cyclohexylene-1,4-diisocyanate, m-phenylene diisocyanate, 3,3'-diphenyl-4,4'-biphenylene diisocyanate, 4,4'-biphenylene diisocyanate, 3,3'-dichloro-4,4'-biphenylene diisocyanate, 1,6-hexamethylenediisocyanate, 1,4-tetramethylene-diisocyanate, 1,10-decamethylenediisocyanate, 1,5-naphthalenediisocyanate, cumene-2,4-diisocyanate, 4-methoxy-1,3-phenylenediisocyanate, 4-chloro-1,3-phenylenediisocyanate, 4-bromo-1,3-phenylenediisocyanate, 4-ethoxy-1,3-phenylenediisocyanate, 2,4'-diisocyanatodiphenylether, 5,6-dimethyl-1,3-phenylenediisocyanate, 2,4-dimethyl-1,3-phenylenediisocyanate, 4,4'-diisocyanatodiphenylether, benzidinediisocyanate, 4,6-dimethyl-1,3-phenylenediisocyanate, 9,10-anthracenediisocyanate, 4,4'-diisocyanatodibenzyl, 3,3'-dimethyl-4,4'-diisocyanatodiphenylmethane, 2,6-dimethyl-4,4'-diisocyanatodiphenyl, 2,4-diisocyanatostilbene, 3,3'-dimethyl-4,4'-diisocyanatodiphenyl, 3,3'-dimethoxy-4,4'-diisocyanatodiphenyl, 1,4-anthracenediisocyanate, 2,5-fluorenediisocyanate, 1,8-naphthalenediisocyanate, 2,6-diisocyanatobenzfuran, 2,4,6-toluenetriisocyanate, and p,p',p''-triphenylmethane triisocyanate.

Suitable initiators useful in preparing prepolymers include propylene glycol, trimethylene glycol, 1,2-butylene glycol, 1,3-butanediol, 1,4-butanediol, 1,5-pentanediol, 1,2-hexylene glycol, 1,10-decanediol, 1,2-cyclohexanediol, 2-butene-1,4-diol, 3-cyclohexene-1,1-dimethanol, 4-methyl-3-cyclohexene-1,1-dimethanol, 3-methylene-1,5-pentanediol, diethylene glycol, 1,2,6-hexanetriol, 1,1,1-trimethylolpropane, 3-(2-hydroxyethoxy)-1,2-propanediol, 3-(2-hydroxypropoxy)-1,2-propanediol, 2,4-dimethyl-2-(2-hydroxyethoxy)methylpentanediol-1,5, 1,1,1-tris[(2-hydroxyethoxy)methyl]ethane, 1,1,1-tris[(2-hydroxypropoxy)methyl]propane, triethanolamine, triisopropanolamine, resorcinol, pyrogallol, phloroglucinol, hydroquinone, 4,6-di-tertiarybutyl catechol, catechol, and orcinol.

#### Use of Additional Materials

Because of the relatively large amount of water used in forming the various dispersions it is possible to combine other materials into the finished sheet. This option is generally not available with systems using a limited amount of water. Useful additives to the water include crosslinkers (especially where the prepolymer is essentially linear), flame retardants, antistats, soil repellents, fungicides, insecticides, stabilizers, fillers, biostats, color additives, organic solvents, blowing agents, dispersing agents, resins, etc. By homogeneously distributing these materials in the aqueous portion of the dispersion, it is possible to distribute the additives widely and uniformly throughout the finished sheet product.

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Useful illustrative examples of materials which may be added include porous structures such as particulate wood fibers; rock wool; glass wool; bagasse; straw; cork; sponge rubber; foamed polystyrene; and the like.

Fire or flame retardant additives usefully included alone or in combination in the aqueous reactant are represented by, for example, zinc borate; calcium carbonate; alum; ferrous sulfate; borax; melamine and boric acid; melamine phosphate; ammonium phosphate; stannic oxide; ammonium sulfate; ammonium sulfamate; titanium and antimony oxides in combination with halide materials and in particular the oxychlorides; aluminum hydrate; ceric hydrate; tetrakis (hydroxymethyl) phosphonium chloride; bromoform and triallyl phosphate; phosphoroxetriamide; chlorinated paraffins; tris (2-ethyl hexyl) phosphate; tris (2,3-dibromopropyl) phosphate, triphenyl phosphate, cresyl diphenyl phosphate; and the like.

The sheet-like materials of the invention retain dimensional stability during wetting and drying cycles and for functional, reinforcing, strengthening, binding, opacifying or cushioning effects; they are useful for various end products such as drapery backing, upholstery backing, blankets, absorptive padding, wall coverings, acoustical panels, protective and/or fire retardant surfaces, apparel, shoe linings, separation membranes, filters and the like. The feature of water vapor permeability of sponges resulting from the hydrophilic nature of the polyoxyethylene polyol reactant renders them attractive for apparel. These present materials are also useful as leather substitutes.

The following examples are presented to illustrate the invention. Examples 1-11 deal with preparation of hydrophilic foams, shredding the foams, dispersing the foam particles in water, and wet-layering the particles to form a sheet. Examples 14-28 deal with formation of foam particles by dispersing a prepolymer into water or an aqueous fiber dispersion followed by wet-layering to form a sheet. Examples 12 and 13 describe prepolymers useful in forming sheets either by the shredding process or by dispersion of the prepolymer into water to provide the foam particles.

#### EXAMPLE 1

To a reaction vessel containing 3,092 grams, representing 1 mole, 3 eq. OH, of a triol prepared from potassium hydroxide catalyzed reaction of 92 grams anhydrous glycerol with 3300 grams of ethylene oxide, were added 522 grams, representing 3 moles, 6 eq. NCO of tolylene diisocyanate having about 80/20 mixture of 2,4 isomer/2,6 isomer. The reaction exotherm was kept at 70.degree. C. by external cooling with water, while stirring for 4 hours. The actual isocyanate content, determined by titration with standard n-butylamine solution in toluene, remained at the constant level of 0.79 meq. NCO/gram relative to a theoretical content of 0.83 meq. NCO/gram. The resultant pale yellow syrup was found to solidify at about 30.degree.-35.degree. C., was soluble in toluene, and acetone, readily reacts with water, and had the following average formula: ##STR1## where n has an average value of about 22. The theoretical molecular weight of the resin product is about 3615.

200 grams of the capped resin having an eq. NCO content of 0.016 was stirred briefly and reacted with 200 grams water. The moles H.sub.2O/NCO groups was 73.2. The reaction mixture was immediately foamed, shredded mechanically to an average particle size to pass through a wire screen of 0.030 inch mesh and wet layered using the paper pulp technique to prepare a bound foam fabric having a thickness when dry of about 0.125 inches. The hydrophilic product was found to have good breathability and comfort characteristics and excellent moisture equilibrium maintenance.

#### EXAMPLE 2

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To a reaction vessel containing 4,136 grams, representing 1 mole, 4 eq. OH, of a tetrol prepared from sodium methoxide catalyzed reaction of 136 grams pentaerythritol with 4400 grams of ethylene oxide, were added 696 grams of tolylene diisocyanate having about 80/20 mixture of 2,4 isomer/2,6 isomer. The reaction was carried out using the procedure of Example 1. The actual isocyanate content noted was 0.86 meq. NCO/gram relative to a theoretical content of 0.83 meq. NCO/gram. The recovered product was a colorless syrup which solidified at about 35.degree.-40.degree. C., was soluble in toluene and acetone, readily reacts with water, and had the idealized average formula: ##STR2## where n has an average value of about 22. The theoretical molecular weight of the resin product is about 4832.

50 grams, of the recovered capped resin product from this example, were reacted with 55 grams water. The moles H.sub.2 O/NCO groups was about 73.2. The foam product was shredded, combined with 7.5 grams cellulosic pulp and 20 grams of acrylic latex. These ingredients were wet layered. Corresponding results to that of Example 1 were realized. It was further noted that the hydrophilic polyurethane interpenetrated the fibers of the fabric and served as a reinforcing binder. The fabric remained soft and pliable.

#### EXAMPLE 3

A solution of 92 grams glycerol and 1000 grams of polyoxyethylene (1000) glycol was outgassed at 100.degree. C. and 10 Torr for two hours. To the outgassed solution was added 870 grams tolylene diisocyanate having an 80/20 mixture of 2,4 isomer/2,6 isomer. The reaction solution was stirred at 60.degree. C. for four hours whereupon the actual isocyanate content reached a constant 2.49 meq. NCO/gram relative to a theoretical content of 2.54. 31.3 parts of the resin product had a theoretical molecular weight of 615.

20 grams of water containing 0.5 grams of antimony trioxide and 5 grams of polyvinyl chloride-latex particles was mixed with 10 grams of the capped resin product having an eq. NCO content of 0.016. The moles H.sub.2 O/NCO groups was 125. The foam so generated was shredded and layered onto a fabric by the procedure of Example 1. The composite product was found to have excellent comfort, fire retardancy and moisture equilibrium maintenance.

#### EXAMPLE 4

The procedure of Example 1 was repeated except that 20 grams of the shredded product was combined with 20 grams of water and 1.5% by weight soft wood paper pulp. The product was characterized with a soft open cell structure which was flexible yet fairly tough and was found to have excellent properties. The weight of pulp employed is based on the weight of the foam particles.

#### EXAMPLE 5

In order to demonstrate use of polyoxyethylene polyisocyanate in making products with attractive colors, a 10 gram portion of the polyoxyethylene tetraisocyanate prepared in Example 2 was mixed with 10 grams of water containing 0.5 gram of Hansa yellow color. A composite having a yellow color and the excellent characteristics of the product of Example 2 resulted.

#### EXAMPLE 6

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In order to demonstrate capping of a polyoxyethylene diol with a polyisocyanate having a functionality greater than 2, to give polyisocyanate foams with higher crosslink density and superior physical properties, lower solubility, and greater hydrolytic stability than products from polyoxyethylene diisocyanates, a 1000 gram portion, of polyoxyethylene glycol of 4000 weight average molecular weight was outgassed at 110.degree. C. and 10 Torr for two hours. Next, to this outgassed liquid was added at 60.degree. C. 200 grams, of polymethylene polyphenylisocyanate commercially available under the name PAPI 901 by Upjohn Co. This latter material has nearly three isocyanate groups per molecule and an isocyanate equivalent weight of 133. A dark reaction solution was noted which was stirred at 60.degree. C. to 70.degree. C. for five hours whereupon the NCO content reached a constant 0.825 meq. NCO/gram relative to a theoretical value of 0.833. The resultant dark product syrup solidified at 45.degree. C. to form a brown, waxy product. Addition of 10 grams of water to 10 grams of the prepared liquid polyisocyanate at 60.degree. C. resulted in a foam and using the procedure of Example 1 gave a resultant tan, soft, flexible, hydrophilic fabric product.

#### EXAMPLE 7

In order to illustrate use of copolymers of 75% ethylene oxide and 25% propylene oxide along with methylene dicyclohexyl diisocyanate to form a triisocyanate that readily reacts with water to give a hydrophilic product, a mixture of 13.4 grams, 0.1 mole of trimethylolpropane and 0.6 grams, 0.01 mole of potassium hydroxide was stirred at 100.degree.-180.degree. C. in the presence of 250 grams of ethylene oxide at 20 to 100 psi. After 3 hours the reaction pressure dropped to one atmosphere. To the reaction product syrup was then added 250 grams of propylene oxide with stirring at 100.degree.-180.degree. C., and a pressure of 20 to 75 psi for 4 hours whereupon the reaction pressure at 100.degree. C. dropped to one atmosphere. To this reaction product syrup having a brown color was added 500 grams of ethylene oxide. The reaction was stirred at 100.degree.-180.degree. C. for 12 hours whereupon the reaction pressure dropped to one atmosphere at 100.degree. C. The resultant brown oil was stripped of volatiles at 50.degree. to 100.degree. C. at 10 Torr resulting with 978 grams of brown syrup having a hydroxyl content of 0.32 meq. OH/gram relative to 0.31 meq/gram theory.

To 931 grams, 0.30 eq. OH of the prepared triol was added 88.0 grams, 0.32 moles, of dicyclohexylmethane diisocyanate. The solution stirred at 60.degree. C. for 8 hours whereupon the NCO content of the polymer reached a constant 0.33 meq./gram relative to 0.32 theory. The triisocyanate product was characterized as a light amber syrup having a viscosity of 12,000 cps at 25.degree. C. (Brookfield).

To a 10 gram portion of the above triisocyanate containing 0.1 gram of silicone surfactant L520 by Union Carbide was added with good mixing 12 grams of water. A product having similar properties to those of the product of Example 1 resulted.

#### EXAMPLE 8

The following substrates were coated on one side by wet layering using the product of Example 3.

Substrate	Size (Cm.)	Average Thickness Foam Pad (mm)
Regular kraft	10 .times. 40	

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		4.5
paper		
Upholstery fabric,		
	10 .times.	40
		4.1
Nylon		
Muslin sheet	10 .times.	40
		5.5
Unbacked, needled		
	20 .times.	40
		4.5
carpet, polypro-		
pylene fiber, (0.05		
g/cm.sup.2 density)		
Rayon nonwoven web		
	10 .times.	40
		3.8
Polyethylene nonwoven		
	10 .times.	40
		3.5
web		

---

## EXAMPLE 9

Sheets were prepared by mixing the shredded foam of Example 1 and additional ingredients as stated in the table below into about 4 liters of water with processing through a "Williams Standard Pulp Testing Apparatus".

Conc.		Latex					
Shredded		Pulp		Asbestos		(Solids)	
						Alum	
HYPOL		Conc.		Conc.		Conc.	
						Conc.	
(g)	(g)	CSF.sup.(1)	(g)	(g)	(g)	Substrate.sup.(2)	
25	25	600	--	--	--	Cheese Cloth	
25	5	600	--	8	--	Nonwoven Polyester	
						Web	
60	5	600	--	--	--		
60	10	520	--	--	--	Upholstry Fabric	
25	--	--	25	7	0.6	--	
50	10	420	--	--	--	--	

.sup.(1) Canadian Standard Freeness

.sup.(2) The wire screen of the Pulp Testing Apparatus was covered by the substrate and the foam sheet formed on the substrate during processing. Corresponding results may be realized.

## EXAMPLE 10

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The procedure of Example 8 was repeated using a 20.times.24 cm. polyamide unbacked carpet except that 30 grams of shredded foam was wet layered.

#### EXAMPLE 11

The procedure of Example 9 was repeated except that a 10.times.40 inch section of muslin sheet was laminated by wet layering with 15 grams of shredded foam.

A 6 mm thick pad of flexible foam laminate resulted; the muslin fabric being integrally bonded. This product was very absorbent of water and was useful as a wiping cloth; similar in effectiveness to chamois. It is also useful as a fabric interliner for wearing apparel, shoe and boot linings and insoles, various types of gas and liquid filters, light weight blankets, mattress covers, coasters, tablecloths, diapers, incontinent pads, upholstery fabrics, mattress ticking, drapery fabrics, sound absorbing wall coverings, vehicle headlining materials, carpet and rug under padding, bathroom and bedroom slippers and the like.

#### EXAMPLE 12

A prepolymer is prepared by admixing trimethylolpropane (TMOP) with polyethylene glycol (PEG - 1,000). The mole ratio of PEG/TMOP was 2:1. The polyol mixture was admixed with sufficient toluene diisocyanate (TDI) to react with about 95% of the hydroxyl groups in the polyol. The reaction was carried out at 60.degree. C. Following the capping reaction a second addition of TDI was made sufficient to react with about 15% of the hydroxyl groups originally present in the polyol, thereby providing a 10% excess of TDI. Following the second addition the reaction mixture was maintained at a temperature of about 60.degree. C. for a two-hour period. The resulting prepolymer is referred to below as Prepolymer 1.

#### EXAMPLE 13

A prepolymer was prepared following the general procedure of Example 12. The PEG/TMOP ratio was 3.33:1 and in the first incremental addition of TDI approximately 93% of theory was employed. In the second addition 12% of theory was employed. The resulting prepolymer is referred to below as Prepolymer 2.

#### EXAMPLES 14-28

The following tables (A-C) illustrate the preparation of sheets by dispersion of prepolymer into water to form foam particles. Dispersion is accomplished by slowly pouring the prepolymer into 7 to 50 times its weight of water while stirring with a standard laboratory mixer. The water may contain additional ingredients such as *asbestos*, wood pulp, or polyester fibers. Examples 19-23 additionally employ latex (GRS - 2,000) and alum. The types of ingredients employed, amounts, and results obtained are set forth in the following tables.

TABLE A

Asbestos.sup.1	
Prepolymer.sup.1	
Prepolymer	
Addition	
Sheet Tensile	

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Example	%	%	Type	Technique	App. Strength.sup.2
---------	---	---	------	-----------	---------------------

14	51.5	48.5	1	A	Slight 25
15	51.5	48.5	1	B	Layering Almost 21
16	51.5	48.5	1	B	Homogen. Homogen. 39
17	51.5	48.5	2	B	Homogen. 10
18	34.7	65.3	2	B	Homogen. very weak

A **Asbestos** and Prepolymer dispersions prepared separately and then mixed.  
 B Prepolymer dispersed directly into dispersion of **asbestos** fibers.  
 .sup.1 The percentages for **asbestos** fibers and prepolymer are based on the combined weight of fibers plus prepolymer.  
 .sup.2 Tensile strength was determined according to ASTM D638.

TABLE B

% .sup.1		% .sup.1		Addition		Sheet Appearance.sup.3		Tensile Strength.sup.2	
Wood									
Example.sup.5		Pulp		Prepolymer		Technique		Addition.sup.4	
								Stiffness	
								Homogeneity	
								Cushioning	
								(psi)	

19	64	36	A	C	1	4	3	346
20	64	36	B	C	3	1	2	217
21	64	36	A	D	4	3	1	34
22	71	29	A	C	2	2	4	345
23	59	41	B	C	1	1	5	548

A Pulp and prepolymer dispersions prepared separately and then mixed.  
 B Prepolymer dispersed directly into pulp slurry.  
 C Latex (GRS 2000) alum added to pulp slurry.  
 D Latex (GRS 2000) alum added to the combined pulp prepolymer slurry.  
 .sup.1 The percentages for wood pulp and prepolymer are based on the combined weight of these materials.  
 .sup.2 Tensile strength was determined according to ASTM D638.  
 .sup.3 Values for stiffness, homogeneity and cushioning were assigned based on manual inspection starting with a rating of 1 for the highest degree of stiffness, homogeneity or cushioning.  
 .sup.4 About 7.5 weight % of latex solids was employed in each run based on the combined weight of pulp, prepolymer and latex.  
 .sup.5 All Examples used Prepolymer 2.

TABLE C

% .sup.1		Relative		Sheet Appearance.sup.3		Tensile.sup.2	
Wood							
Pulp							

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%.sup.1										
%.sup.1										
Total										
Williams										
Prepolymer										
Stiff-										
Homo- Strength										
Example.sup.4										
Fibers										
Polyester										
Prepolymer										
Charge										
Freeness										
Type ness.										
geneity										
Cushioning										
(psi)										
20	64	0	36	1	8	2	2	2	4	217
23	59	0	41	0.87	8	2	1	1	5	548
24.sup.6										
	51	13	36	1	8	2	3	4	2	177
25	38	26	36	0.5	7	2	4	5	3	184
26	43	29	29	0.45	7	2	--	--	--	---.sup.5
27	38	26	36	0.5	5	2	5	3	1	140
28	38	26	36	0.5	5	1	--	--	--	---.sup.5

.sup.1 The % is based on the combined weight of pulp, polyester fibers and prepolymer employed.

.sup.2 Tensile strength was determined according to ASTM D638.

.sup.3 Values for stiffness, homogeneity and cushioning were assigned based on manual inspection starting with a rating of 1 for the highest degree of stiffness, homogeneity or cushioning.

.sup.4 Examples 20 and 23 are repeated from the preceding table.

.sup.5 As illustrated by Examples 26 and 28 it may be necessary to adjust the fiber mix employed to include less polyester fibers if a coherent sheet is to be obtained.

.sup.6 In Examples 24-28 the prepolymer is dispersed directly into a dispersion of the fibers.

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## United States Patent Office

3,555,122

Patented Jan. 12, 1971

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**MIXTURE OF A SUSPENSION RESIN OF VINYL CHLORIDE AND AN ORGANOSOL RESIN OF VINYL CHLORIDE**

Charles W. Simons, Bedford, Mass., assignor to W. R. Grace &amp; Co., Cambridge, Mass., a corporation of Connecticut

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U.S. Cl. 260-899

2 Claims

**ABSTRACT OF THE DISCLOSURE**

A plastisol composition particularly suited for use in sealing container closures and containing (1) a mixture of a suspension resin of a vinyl chloride polymer and an organosol resin of a vinyl chloride polymer and (2) a liquid non-volatile plasticizer for the resin mixture (e.g. dioctyl phthalate). The organosol resin is present in an amount between about 5 and 30% by weight of the resin mixture.

This invention relates to plastisol compositions, and in particular, it relates to plastisol compositions having a resin component containing a very substantial proportion of coarse resin.

Plastisol compositions have been used in the preparation of films and coatings, rainwear, printing plates, closure gaskets for hermetically sealing glass containers and in the manufacture of a wide variety of other products. Conventionally, plastisol compositions are defined as dispersions of finely divided thermoplastic resin particles in a liquid, non-volatile plasticizer in which the resin is insoluble at room temperature. However, at elevated temperatures the resin particles are substantially completely solvated by the plasticizer so that a homogeneous solution is obtained which is transformed into a rubbery, thermoplastic gel upon cooling.

In preparing plastisols, it is customary to use resins, such as vinyl chloride polymer resins, which have been prepared specifically for this purpose by aqueous emulsion polymerization followed by spray drying. These resins are characterized by excellent "stir-in" properties so that they can be readily dispersed in a liquid plasticizer at room temperature to form a paste-like mixture. The plastisol grade resins conventionally employed are high molecular weight homopolymers of vinyl chloride and copolymers of vinyl chloride with up to about 20% by weight and preferably, less than 5% by weight of vinyl acetate or other copolymerizable monomer. Typically, these resins have an inherent viscosity above about 1.10 and a particle size in the range of about 0.1 to 4.0 microns with the average number particle diameter ranging between about 0.2 and 2.0 microns.

Due to their method of manufacture, plastisol grade resins contain relatively large amounts of water-extractable soaps. For this reason, suspension grade resins which are essentially free from soap have been used in admixture with plastisol grade resins in applications where the presence of large amounts of water-extractable soap is undesirable. By suspension resin is meant vinyl resins, such as vinyl chloride polymer resins, produced by sus-

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pension polymerization techniques known to the art. The suspension resins, like the plastisol resins, may be homopolymers of vinyl chloride or copolymers of vinyl chloride but in comparison to plastisol resins have a considerably larger particle size and vary more widely in molecular weight from relatively low to relatively high molecular weight. Also, suspension resins do not possess the stir-in characteristics found in plastisol grade resins.

One application where blends of suspension and plastisol grade resins have been used is in the manufacture of fluxed plastisol sealing gaskets for container closures. Because the soaps present in plastisol resins are readily extracted from the gaskets and because the extracted soaps tend to impart an off-flavor to the food pack, a suspension resin is substituted for part of the plastisol resin to improve the taste characteristics of the gasket. While some taste improvement is obtained, any further improvement is limited by the proportion of suspension resin which can be employed to give a still usable composition after normal storage times. Because the suspension resin is coarse, it settles out of dispersion within a few hours, and upon prolonged standing, the settled resin particles become hard packed and difficult to redisperse. As a result, the quantity of suspension resin ordinarily used in admixture with the plastisol resin is not more than about 35% by weight and is usually less than 30% by weight as based on the combined weight of plastisol and suspension resins.

It is, therefore, an object of the present invention to prepare plastisol compositions wherein settling of the resin component is reduced and any settled resin can be readily redispersed after prolonged standing though the resin component contains a higher proportion of coarse suspension grade resin than previously employed. It is a further object of the present invention to provide plastisol compositions wherein the resin component remains substantially completely suspended over comparatively long periods. These and other objects are accomplished by using certain organosol grade resins rather than plastisol grade resins in admixture with the coarse suspension resin to form the resin component.

More specifically, the present invention provides plastisol compositions comprising (1) a vinyl chloride resin mixture composed of (a) a suspension resin and (b) an organosol resin having an average number particle diameter below about 0.25 micron and an inherent viscosity less than 0.90, and (2) a liquid, non-volatile plasticizer for said resin mixture, said organosol resin being used in an amount of at least about 5% by weight of said resin mixture. In a preferred composition of the present invention, the organosol resin constitutes between about 10 and 30% by weight of the vinyl resin mixture.

The term "organosol grade resin" is used herein to denote vinyl resins having a very fine particle size produced in the same manner as plastisol grade resins, i.e., by aqueous emulsion polymerization techniques as is well-known in the art. These resins, though useful in plastisol compounding, are manufactured in very finely divided form especially for use in fluid dispersions similar to plastisols except that the resin particles are dispersed in a liquid medium containing a volatile diluent in addition to the liquid non-volatile plasticizer for the

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resin. Such dispersions are commonly referred to as "organosols."

The organosol grade resins used in carrying out the present invention may be homopolymers of vinyl chloride or copolymers of vinyl chloride with about 5% by weight or less of vinyl acetate, acrylonitrile, vinylidene chloride, dialkyl maleate, or other ethylenically unsaturated monomer copolymerizable therewith. However, to obtain the benefits of the present invention, the organosol resin employed should have a relatively low molecular weight such that its inherent viscosity is less than 0.90 and should have an average number particle diameter less than about 0.25 micron. Typical of the organosol grade resins which may be used in formulating the present compositions is "Geon 126," a homopolymer of vinyl chloride having an average number particle diameter of about 0.2 micron and an inherent viscosity of about 0.80.

By the term "inherent viscosity" is meant the ratio of the natural logarithm of the relative viscosity to the concentration of vinyl chloride polymer in cyclohexanone as determined according to the procedure outlined in ASTM D1243-60 Method A. The viscosity values obtained by this method are related to the average molecular size of that portion of the polymer which dissolves in the cyclohexanone solvent. All values for inherent viscosity given herein are based on the above standard test.

Any of the suspension grade resins conventionally used in the art may be employed in the present invention including both homopolymers of vinyl chloride and copolymers of vinyl chloride containing 20% by weight or less of vinyl acetate, chloroethylene or other ethylenically unsaturated monomer copolymerizable therewith. In general, these resins have a particle size in the range of approximately 30 to 300 microns with the average number particle diameter being between about 80 and 180 microns and have an inherent viscosity between about 0.50 and 1.20. Illustrative of suspension grade resins which may be used in preparing the present compositions are homopolymers of vinyl chloride, such as "Geon 101," "Vinylite QYNA," "Marvinol VR-10," "Exon 500," and copolymers of vinyl chloride, such as "Geon 202" (94% vinyl chloride copolymerized with 6% vinylidene chloride), "VC-265" (95% vinyl chloride copolymerized with 5% vinyl acetate), and "Vinylite VYNW" (96% vinyl chloride copolymerized with 4% vinyl acetate).

Among the plasticizers which may be used in preparing the present compositions are dialkyl phthalates, alkyl phthalyl alkyl glycolates, dialkyl esters of alkane dicarboxylic acids, acetyl trialkyl citrates, and trialkyl and triaryl phosphates. Particular plasticizers which may be employed include dioctyl phthalate (di-2-ethylhexyl phthalate), octyl decyl phthalate, ethyl phthalyl ethyl glycolate, butyl phthalyl butyl glycolate, diisobutyl adipate, dibutyl sebacate, acetyl tributyl citrate, trioctyl phosphate and tricresyl phosphate. Other useful plasticizers include alkyl esters of fatty acids, such as octyl stearate; epoxy derivatives, such as epoxidized soybean oil; and polymeric polyester plasticizers, such as, polyethylene glycol adipate. While any of the primary plasticizers may be used alone, mixtures of primary plasticizers may be employed, and also, mixtures of one or more primary plasticizers with one or more secondary plasticizers may be used.

Besides the resin and the plasticizer, the compositions of the present invention may contain other conventional compounding ingredients. Such ingredients include fillers, e.g., whiting, talc, clays, barytes, asbestine; pigments, e.g., carbon blacks, iron oxides, titanium dioxide; and stabilizers, e.g., zinc and calcium stearates, thio-organic tin compounds, cadmium and barium laurates. Other compounding ingredients which may be used are waxes, e.g., stearyl alcohol, polyamide wax, paraffin and microcrystalline waxes; wetting agents, e.g., zinc resinate, polyethylene glycol fatty acid esters; and blowing agents, e.g., azodicarbonamide, dinitrosopentamethylenetetramine, and 3,3'-disulphonylhydrazide diphenylsulphone.

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To obtain a composition where the settling of coarse resin is considerably reduced and where the settled resin remains soft and readily redispersible, the amount of organosol grade resin used in admixture with the suspension grade resin should be at least 5% by weight of the total resin used. Below 5% by weight organosol resin, the coarse suspension resin which settles becomes hard packed and difficult to redisperse. In a preferred embodiment, the organosol grade resin is used at a level of at least 10% by weight of the resin component so that a plastisol composition substantially free from resin settling is obtained. The maximum quantity of organosol resin used is not critical with respect to preventing settling of coarse resin but depends upon other considerations, such as viscosity. For most applications, the practical maximum limit for organosol resin as based on acceptable viscosity characteristics is about 30% by weight of the resin component. Also, plastisol compositions containing larger amounts of organosol resin tend to gel during normal storage times.

With the exception of the proportion of organosol and suspension resins in the resin component, the total amount of resin and the amount of plasticizer and other ingredients used may vary widely. On the basis of 100 parts by weight resin, the plasticizer may be used in amounts ranging between about 50 and 250 parts by weight, and the filler may vary between about 0 to 150 parts by weight. When stabilizers, waxes, wetting agents and other compounding ingredients are employed they are used in conventional amounts to achieve the properties desired during processing and in the fluxed composition.

The following examples are given to more clearly illustrate the present invention. All quantities given are in parts by weight unless otherwise specified.

#### EXAMPLES 1-9

Two series of compositions were made to compare the settling characteristics of different resin components dispersed in plasticizer. One series of compositions representing Examples 2-5 contained a resin component composed of a mixture of coarse suspension grade resin and a plastisol grade resin in varying amounts. The other series of compositions representing Examples 6-9 contained a resin component composed of varying amounts of an organosol grade resin in admixture with a coarse suspension resin. Example 1 containing only suspension resin in the resin component served as the control.

The particular ingredients used and their proportions are given in Table I below.

TABLE I

Ingredients	Example No. (parts by weight)								
	1	2	3	4	5	6	7	8	9
Polyvinyl chloride <sup>1</sup>	100	95	90	80	60	95	90	80	60
Polyvinyl chloride <sup>2</sup>		5	10	20	40				
Polyvinyl chloride <sup>3</sup>						5	10	20	40
Dioctyl phthalate <sup>4</sup>		70	70	70	70	70	70	70	70

<sup>1</sup> Suspension resin, average number particle size 80 $\mu$ ; inherent viscosity 0.75.

<sup>2</sup> Plastisol resin, average number particle size 0.53 $\mu$ ; inherent viscosity 1.27.

<sup>3</sup> Organosol resin, average number particle size 0.21 $\mu$ ; inherent viscosity 0.80.

<sup>4</sup> Plasticizer.

The particle size of the resins employed was determined by microscopic examination and is given in microns ( $\mu$ ). The inherent viscosity of the resins was determined in cyclohexanone solution according to the standard test described in ASTM D1243-60, Method A.

The composition of Examples 1 to 9 were prepared by adding the resin or resins to the plasticizer with stirring. After uniform dispersions were obtained, the compositions were allowed to stand at room temperature for one month after which time the amount of settling in each composition was observed. The results obtained in terms of amount of settling and the relative hardness and redispersibility of the settled mass are given in Table II below.

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TABLE II

	Example No.								
	1	2	3	4	5	6	7	8	9
Plastisol grade resin (wt. percent total resin)	5	10	20	40	5	10	20	40	
Organosol grade resin (wt. percent total resin)	Severe	Severe	Severe	Heavy	Moderate	Moderate	Very slight	None	None
Amount of settling (after 1 month)	Hard	Hard	Hard	Moderately hard	Moderately hard	Soft	Soft		
1. Degree of packing and	N	N	N	N	N	R	R		
2. Redispersibility of settled resin <sup>2</sup> (after 1 month)									

<sup>1</sup> Gelled after 1 month.<sup>2</sup> N—Not easily redispersed; R—Easily redispersed.

From the results tabulated above, it is apparent from Examples 6 to 9 that as little as 5% by weight of organosol grade resin in the resin component is effective in reducing the amount of resin settling. At a level of 10% by weight, settling was negligible and at the 20 and 40% levels, there was none. Further, any resin that settled from the dispersion formed a soft mass which could be brought back into dispersion with very little stirring.

In comparison, the compositions of Examples 2 to 5 containing plastisol grade resin showed considerably more settling than Examples 6 to 9 at the 5, 10, 20 and 40% levels, respectively. At 5 and 10% by weight plastisol grade resin, settling was excessive, and the compositions showed no improvement over the control while at 20 and 40% settling still remained substantial. Also, the settled mass in each of the Examples 2 to 5 was hard or moderately hard packed so that the settled resin was difficult to redisperse even with long and careful stirring.

## EXAMPLE 10

In a further comparison, a plastisol composition was formulated which was identical to Example 3 above except that the plastisol grade resin used was a copolymer of 95% by weight vinyl chloride and 5% by weight vinyl acetate. Also, this plastisol resin though having a relatively high molecular weight as reflected by its inherent viscosity of about 1.27, had a comparatively fine particle size. The average number particle diameter was about 0.22 microns.

The composition of Example 10 was prepared in the same manner as Examples 1 to 9 by adding the plastisol and suspension resins to the plasticizer and stirring until a homogeneous dispersion was obtained.

After mixing, the composition was allowed to stand at room temperature for one month. At the end of this time, it was observed that heavy settling had occurred and that the settled resin was hard packed and difficult to redisperse.

## EXAMPLE 11

Another composition was prepared as described in Examples 1 to 9 above. The ingredients employed and their amounts were as follows:

Ingredients:	Parts by weight
Copolymer of 94% vinyl chloride and 6% vinylidene chloride (suspension resin—ave. No. particle size—125 $\mu$ ; inherent viscosity—0.87)	90
Polyvinyl chloride (organosol resin—ave. No. particle size 0.21 $\mu$ ; inherent viscosity 0.80)	10
Diocetyl phthalate (plasticizer)	70

The above composition when observed after standing at room temperature for several months showed only slight settling. Also, the settled resin remained soft and was easily redispersed with very little stirring.

From the above examples and results obtained, it is evident that settling of coarse suspension resins from a

plastisol composition can be greatly reduced and eliminated, if desired, by using comparatively small amounts of certain organosol grade resins in admixture with a coarse suspension resin to form the resin component. Specifically, the organosol grade resins which provide these advantages are those which have an average number particle diameter below about 0.25 micron together with an inherent viscosity of less than about 0.90. Besides keeping most of the coarse resin in suspension, any resin that does settle in the presence of the organosol grade resin remains easily redispersible after prolonged standing.

Because the resin component tends to remain evenly dispersed over long periods, very little if any stirring of the plastisol is required at the time of use, and constant or intermittent stirring during application as previously required is unnecessary. When it is desired to prepare thick films and coatings or other thick products, there is no separation or stratification of the resin between the time of application and fluxing so that cured products having a uniform distribution of resin and plasticizer are consistently obtained. Moreover, the compositions of the present invention make the preparation of fluxed products, such as fluxed closure gaskets, containing a negligible amount of extractable soap commercially practical since the compositions remain usable indefinitely despite the exceedingly large proportion of suspension resin.

I claim:

1. A plastisol composition consisting essentially of (1) a vinyl resin mixture composed of (a) a resin of a vinyl chloride polymer having an average number particle diameter between about 80 and 180 microns and an inherent viscosity between about 0.5 and 1.20 and (b) a resin of a vinyl chloride polymer having an average number particle diameter below about 0.25 micron and an inherent viscosity below about 0.90, and (2) a liquid non-volatile plasticizer for said resin mixture, said resin (b) being used in an amount of at least about 5%, up to about 30% by weight of said mixture.

2. A composition according to claim 1 wherein said resin (b) is polyvinyl chloride having an average number particle diameter of about 0.21 micron and an inherent viscosity of about 0.80.

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MURRAY TILLMAN, Primary Examiner

C. J. SECCURO, Assistant Examiner

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## GASKET-FORMING COMPOSITIONS FOR CLOSURE ELEMENTS

Charles W. Simons, Bedford, Mass., assignor to W. R. Grace & Co., Cambridge, Mass., a corporation of Connecticut

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5 Claims

### ABSTRACT OF THE DISCLOSURE

Compositions suitable for use as gaskets in container closure elements consisting of a two-phase system composed of plasticized coarse resin particles dispersed in water. Thickening agents such as water-insoluble materials, e.g., silica gel, or water-soluble materials, e.g., cellulose derivatives, may be included in the compositions.

This invention relates to compositions which are suitable for forming sealing gaskets for container closures.

Vinyl resin plastisols are currently employed to form gaskets in a variety of closures, such as crowns, screw caps, lug caps, etc. to seal containers and preserve the contents thereof. Plastisols are composed essentially of a resin dispersed in a liquid non-volatile plasticizer in which the resin is essentially insoluble at room temperature but is rapidly soluble at an elevated temperature. Gaskets are formed by depositing a predetermined amount of plastisol in a closure and heating the closure containing the plastisol at a temperature between about 325° F. and 425° F. whereby the resin fuses with the plasticizer. Upon cooling, the fused mass forms a coherent rubber-like gasket.

In one method, a gasket is formed by depositing a metered amount of plastisol in the center of an inverted closure shell, such as a crown, and the shell is spun to distribute the plastisol over the panel area. In another method, the deposited plastisol may be distributed and molded to the desired shape by applying a plunger which may or may not be heated.

Vinyl chloride polymers are generally selected as the resin component in plastisols because of their inert characteristics. These polymers are frequently referred to as dispersion or paste grade resins and are prepared by emulsion polymerization whereby a particle size sufficiently small to remain in colloidal suspension is produced. Careful control of particle size is essential to yield resins which will form plasticizer dispersions with optimum rheological properties. The particle size generally ranges between 0.2 and 5 microns.

Emulsion polymerization comprises four ingredients: (1) monomer, vinyl chloride, for example; (2) continuous phase (water); (3) emulsifying agent (soap, for example, sodium dodecyl benzene sulfonate); and (4) initiator (for example, sodium peroxydisulfate). In this system, the monomer is emulsified in the water with the aid of the soap and the monomer is present almost entirely as emulsion droplets dispersed in a continuous aqueous phase. When sufficient soap is added to the water, it exists in the form of micelles. Part of a monomer added to the system enters the micelles, but most of it exists in the form of droplets about a micron in diameter stabilized by a portion of the soap. As free radicals are formed, they migrate into the monomer phase where polymerization takes place. As the polymer is formed, the micelles grow by the addition of monomer from the aqueous phase and eventually from the monomer droplets.

When polymerization is complete, the dispersed particles are then dried by spraying the emulsion into a

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current of hot air. The resulting particles consist of agglomerates which range in size up to 5 microns and are composed of individual spheres having a size of about 0.2 to 0.5 microns. Additional soap may be added prior to spray drying to improve the dispersion characteristics of the dried resins.

The use of highly effective surface-active agents in emulsion polymerization yields a polymer having a high molecular weight and a particle size of less than about five microns. The particle size represents an advantage for use in plastisols because the polymer is easily stirred with the plasticizer to form a uniform mixture. The high molecular weight prevents solvation of the polymer by the plasticizer at room temperature, thus assuring viscosity stability of the plastisol during storage. However, because of the very small particle size a great surface is exposed on which the soap is adsorbed. This is a definite drawback because the soap represents an impurity, and gaskets formed from plastisols containing a polymer derived by emulsion polymerization adversely affect the flavor of certain edible products. Carbonated beverages, for example, are sensitive to flavor deterioration. In addition, the soap impairs the clarity of clear gaskets formed from such plastisols.

It is, therefore, an object of this invention to provide sealing compositions which avoid the drawbacks associated with gaskets formed of polymers containing residual contaminants resulting from emulsion polymerization. This objective is achieved by providing a composition which is substantially immobile at room temperature and consists of a two-phase system comprising plasticized coarse resin particles dispersed in water. The viscosity of the composition is regulated by amount of water employed as the continuous phase in the presence or absence of a thickening agent. Various additives may be included in the composition to impart desirable properties, such as stabilizers, colorants, etc.

Although the sealing composition of this invention includes a plasticized resin, it differs from the generally accepted definition of plastisols. In this invention, a substantial portion of the plasticizer is absorbed by the resin particles, and the plasticized resin together with the unadsorbed plasticizer and some resin particles remain in a dispersed state at room temperature in the aqueous medium until the composition is fused. During fusion the water is driven off and the plasticizer is completely absorbed during the fusion cycle. In a true plastisol, however, the resin is dispersed in the liquid plasticizer at room temperature.

This invention, therefore, permits the use of thermoplastic resins in gasket-forming compositions which are available in granular form but which cannot be used in making plastisols because of the large particle size of the resin. For example, a terpolymer of vinyl chloride, vinyl acetate and maleic anhydride can be used in the aqueous compositions of this invention without difficulty. On the other hand, if this terpolymer were employed in a plastisol it would have poor paste viscosity stability because the terpolymer would be rapidly swollen by the plasticizer. One advantage of using this terpolymer is that it imparts superior adhesion to metals and thus functions as an excellent gasketing material in metal closures. In addition, the resins are generally formed by suspension polymerization techniques which are not dependent on the use of emulsifying agents, and are, therefore, free of emulsifier contamination.

The coarse resins used in this invention are more economical to prepare than the fine resins used in plastisol preparation. They are made by suspension polymerization in which the monomer is suspended as small droplets in a medium (generally water) in the presence

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a suspending agent, such as polyvinyl alcohol or magnesium phosphate, and an oil-soluble catalyst, such as benzoyl peroxide. With suitable control, the particle size of the resin ranges between about 20 and 200 microns. On the other hand, the particle size of the resin derived by emulsion polymerization and which is customarily employed in plastisol compositions ranges between about 0.2 and 5 microns with an average particle size of about 1.5 microns.

The single figure of the drawing diagrammatically illustrates the essential steps which are followed to mold gaskets from compositions of this invention.

In preparing the compositions of this invention, the steps may be varied without significantly affecting their final properties. In one method, a master batch is prepared containing sufficient water-miscible thickening agent and water to form a four percent solution which is subsequently diluted with additional water to provide the desired viscosity of the composition. The other ingredients such as plasticizer, stabilizer, etc. are then thoroughly stirred into the solution. Finally the resin is added and is thoroughly mixed with the other ingredients. In an alternate method, the liquid plasticizer may be mixed with the resin and then added to the aqueous system. Irrespective of the manner in which the resin and plasticizer are added, ultimately a substantial portion of the plasticizer is absorbed by the coarse resin particles. The final gasket-forming composition is a slurry which resembles a gritty sand-water mixture in which the resin particles containing the absorbed plasticizer, the unabsorbed plasticizer, small amounts of resin particles, other solid additives, and all hydrophobic liquids represent the discontinuous phase. The water together with a water-soluble thickening agent define the continuous phase. The viscosity ranges between about 500 and 40,000 centipoises, as measured on a Severs Rheometer, Model A-120 under the following conditions:

Length of orifice—5 cm.

Radius of orifice—0.1564 cm.

Efflux time—5 seconds

Applied gas pressure—5 to 150 p.s.i.

The compositions of this invention are well suited for molding gaskets in closures by means of a shaping die. In a molding operation as illustrated in the drawing, a predetermined amount of composition 11 is delivered from a suitable source, such as a dispensing nozzle 12, and placed in the center portion of the crown 10. The crown containing the composition is then moved to a heating chamber, such as oven 13, in which air heated to a temperature ranging between about 325° F. and 425° F. is circulated. As the composition is heated, the water is volatilized, and continued heating to higher temperatures causes fusion of the resin and plasticizer. The crown containing the fused mass is then delivered to a molding station where it is shaped into a gasket. The molding station includes a platen 14 having a groove 15 arranged below a shaping member comprised of a shank 16 and a die 17. Either or both the platen and the shaping member may be cold or heated (by means not shown) below the fluxing temperature of the composition. Subsequently, the closure is cooled whereupon the gasket is solidified to a coherent mass.

In preparing the gasketed closure, a sheet of metal plate, such as tinplate, aluminum or aluminum alloy, is provided. Since metallic contamination has the most drastic action on palatability of edible products, such as carbonated beverages, the metal surface is first coated with a lacquer or enamel to protect the contents in the container against such contamination. When the gasket is formed of a composition which includes a vinyl chloride resin, it is usual to coat the metal with a compatible vinyl lacquer to assure adhesion of the gaskets to the coating. The coating may be one which is derived from a lacquer containing a vinyl resin alone or in combina-

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tion with one or more of oleoresinous, epoxy, acrylic or phenolic components. A satisfactory coating composition is one derived from polyvinyl chloride or a major amount of vinyl chloride copolymerized with up to about 20% by weight of vinyl acetate in combination with the aforementioned components.

Vinyl resins are particularly suitable for use in the sealing compositions of this invention. These include coarse homopolymers of vinyl chloride and copolymers of vinyl chloride with up to 20% by weight of another monomer copolymerizable therewith. Suitable monomers include acrylonitrile, vinylidene chloride, vinyl acetate, and dialkyl maleates. Typical copolymers include 95 percent vinyl chloride-5% vinyl acetate; 95 percent vinyl chloride-5% dialkyl maleate; and 94 percent vinyl chloride-6% vinylidene chloride. The preferred resin is polyvinyl chloride. These polymers are prepared by suspension polymerization and are substantially free of emulsifying agents.

The plasticizer must be capable of dissolving the resin when heated, and it must remain completely compatible with it upon cooling. Illustrative plasticizers include dialkyl phthalates, alkyl phthalyl alkyl glycolates, dialkyl esters of alkane dicarboxylic acids, acetyl trialkyl citrates, and trialkyl and triaryl phosphates. Particular plasticizers include dioctyl phthalate (di-2-ethylhexyl phthalate), octyl decyl phthalate, ethyl phthalyl ethyl glycolate, butyl phthalyl butyl glycolate, diisobutyl adipate, dibutyl sebacate, acetyl dibutyl citrate, trioctyl phosphate and tricresyl phosphate. Other useful plasticizers include alkyl esters of fatty acids, such as octyl stearate; epoxidized triglycerides, such as epoxidized soybean oil; and polymeric polyester plasticizers, such as polymeric glycol adipate. The amount of plasticizer in the composition ranges between about 20 and 250 parts, preferably 20 to 150 parts by weight per hundred parts by weight of resin.

The type and amount of thickening agent influence the viscosity and flow characteristics of the composition. If the viscosity is too low, it may create settling problems during storage, and if it is too high it may not be satisfactorily metered into closures through dispensing nozzles. Therefore, by judicious selection of the thickening agent and the quantity employed, a composition is obtained which is a gritty paste having limited radial mobility and which remains substantially in place when deposited in the center of an inverted closure, but which is easily distributed over the panel during the molding step. The amount of thickening agent which achieves these results ranges between about 0.03 and 10 parts by weight per hundred parts by weight of resin.

Satisfactory thickening agents include materials which are insoluble in water, such as finely divided silica gel, fuller's earth, activated clay, activated alumina and similar absorbents which take up liquids on their surface. The preferred thickeners are those which are water-soluble at room temperature as these agents contribute to the continuous phase of the compositions and enable thorough and uniform mixing of the solid ingredients. Illustrative agents are cellulose derivatives, such as alkali metal salts of carboxymethyl cellulose, for example, sodium carboxymethyl cellulose and potassium carboxymethyl cellulose; methyl cellulose; hydroxymethyl cellulose; hydroxy propyl cellulose, and mixtures of such cellulose derivatives. Other agents include ethylene oxide polymers.

The thickening agent may be excluded from the composition provided that the composition is maintained in a circulated condition and is used immediately to form gaskets. If the agent is omitted and the composition is not circulated, settling of the components will occur with the result that the gaskets will lack uniform properties.

The composition may also include a solid decomposable chemical blowing agent to provide the gasket with a cellular structure in the annular region 18 which contacts the

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lip of a container. During the fluxing cycle, the blowing agent decomposes and releases a gas whereby cells 19 are formed in the mass. The particular gasket design may be achieved by using a die 17 having a flat or convex center portion 20 on its face and a peripheral channel 21. During the molding step, the die will compress the cells which form in the center of the gasket while preserving the cellular structure in the annular area by means of the peripheral channel. Suitable blowing agents include azodicarbonamide, 3,3'-disulphonhydrazido diphenylsulfone, dinitrosopentamethylene tetramine, diazoaminobenzene, and p,p'-oxybis (benzene sulfonyl hydrazide). The amount of blowing agent which will provide the desired cellular structure ranges between about 0.2% and 5.0% based on the weight of the resin.

Various other additives may be included to modify the compositions. These include fillers, such as anhydrous calcium sulfate, talc, wood flour and asbestos; stabilizers, such as tetrasodium pyrophosphate, tribasic lead silicate, calcium stearate, zinc stearate, dibasic lead stearate and organotin complexes; and pigments, such as carbon black, titanium dioxide and alumina powder. Small amounts of emulsifier of the order of less than 2% based on the weight of the resin may be added to aid in dispersing the free plasticizer.

The invention is further illustrated by the following examples:

## EXAMPLE 1

A sealing composition was prepared which included the following ingredients:

Ingredient:	Parts by wt.
Polyvinyl chloride (Geon 103 EP) <sup>1</sup> .....	100
Hydroxy propyl cellulose (thickening agent) ..	1
Diocetyl phthalate (plasticizer) .....	96
Epoxidized soya bean oil (plasticizer) .....	10
Mixed calcium and zinc stearates (stabilizer) ..	1
Water .....	65

<sup>1</sup> Suspension grade resin having a particle size of less than 10% ranging between 75 and 130 microns and less than 90% ranging between 130 and 200 microns, all particles passing through a 42-mesh screen (Tyler Standard Scale).

The composition was prepared by first dissolving the hydroxyl propyl cellulose in the water and thereafter incorporating the plasticizers and stabilizer. The polyvinyl chloride was finally added to the system while thoroughly agitating the same. The result was a viscous fluid having the consistency of wet sand.

330 milligrams of the composition were deposited in the center of a crown closure and the closure containing the composition was then passed to an oven in which air heated at 400° F. was circulated. The residence time in the oven was 133 seconds at which time the water was driven off and the composition was fluxed. The fluxed composition exhibited little or no radial movement. A gasket was then molded over the panel of the closure using a die having a temperature of 78° F. and a platen having a temperature of 320° F. The die pressure was 80 p.s.i., and the molding cycle was completed within 4 seconds. The result was a coherent gasket which adhered well to the closure.

## EXAMPLE 2

A composition was prepared in the same manner as described under Example 1 and was composed of the following ingredients:

Ingredient:	Parts by wt.
Geon 103 EP .....	100
Hydroxy propyl cellulose .....	1
Epoxidized soya bean oil .....	240
Mixed calcium and zinc stearates .....	1
Water .....	65

330 milligrams of the composition were placed in a crown closure and then moved to an oven in which air heated to 400° F. was circulated. The residence period was

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one minute during which time the water was driven off and the composition was fluxed. The fluxed composition was then molded in the crown with a die having a temperature of 75° F. and a platen temperature of 75° F. The gasket was completely molded within four seconds, and it was of acceptable quality.

## EXAMPLE 3

In another embodiment, the sealing composition of this invention was prepared as described in Example 1. It was composed of the following ingredients:

Ingredient:	Parts by wt.
Polyvinyl chloride (Escambia 2225) <sup>1</sup> (Suspension grade resin) .....	100
Di(n-hexyl)azolate .....	60
Dibutyl tin dilaurate .....	5
Sodium lauryl sulfate (35% solution in water) ..	6
Ethylene oxide polymer, molecular weight about 600,000, 10% solution in water (thickening agent) .....	20
Water .....	35

<sup>1</sup> Particle size (U.S. Standard Scale).

Mesh No.	Percent retained
25 45 .....	2
50 .....	6
60 .....	36
80 .....	40
200 .....	16

320 milligrams of the composition were placed in a crown and heated in an air stream for two minutes at 420° F. The resulting fluxed composition was then molded for four seconds using a die and platen, each having a temperature of 75° F. The gasket was clear and conformed to the inside surface of the crown covering the panel area.

## EXAMPLE 4

The following example shows that satisfactory sealing compositions can be prepared using plasticizers which are unsuitable in plastisol formulations. Experience in plastisol formulations showed that 50 parts per hundred parts of resin of the plasticizer employed in this composition yielded plastisols which were very viscous and completely unusable. In addition, when the plasticizer content was increased to 100 parts by weight of resin a heavy sticky plastisol resulted. A satisfactory composition, however, was prepared according to the procedure described in Example 1 and was composed of the following ingredients:

Ingredient:	Parts by wt.
Geon 103 EP .....	100
Paraplex G25 (polyester type plasticizer) .....	50
Emcol 14 (polyglycerol oleate) (wetting agent) ..	1
Hydroxy propyl cellulose .....	2
Water .....	108

To facilitate mixing, the composition was heated to about 120° F. before the resin was stirred in. Although the final mixture was quite thick, it could be distributed through conventional dispensing equipment. 350 milligrams of the composition were deposited in a crown and heated at 420° F. for four minutes. An acceptable gasket was formed in place using a cold (room temperature) die and a platen heated at 200° F.

## EXAMPLE 5

This example illustrates formation of an annular gasket in a 48-millimeter continuous thread cap. The composition was prepared according to the procedure described in Example 1 and was composed of the following:

Ingredient:	Parts by wt.
Geon 103 EP .....	100
Hydroxy propyl cellulose .....	1
Diocetyl phthalate .....	69
Epoxidized soya bean oil .....	21

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Ingredient:	Parts by wt.
Mixed calcium and zinc stearates	1
Water	65

A ring of the composition was deposited in the annulus of the threaded cap which was internally coated with a vinyl lacquer. The cap containing the annular deposit was heated in an oven at 430° F. for 1½ minutes and then molded with a cold die designed to compress the ring. The result was an acceptable well-adhered gasket.

The gasket-forming procedure was varied in a further embodiment by employing the composition of Example 5 but omitting the molding step. Upon fluxing, a slightly cellular gasket resulted which adhered well to the protective lacquer coating. This type of gasket is useful when sealing at low application torques is required.

## EXAMPLE 6

This example illustrates the use of low amounts of plasticizer to produce acceptable gaskets. It was prepared in the manner described under Example 1 and was composed of the following ingredients:

Ingredient:	Parts by wt.
Geon 103 EP	100
Hydroxy propyl cellulose	1
Epoxidized soya bean oil (plasticizer)	10
Octyl diphenyl phosphate (plasticizer)	20
Mixed calcium and zinc stearates	1
Water	65

The following conditions were employed to form a gasket in a crown using 330 milligrams of composition:

## Fluxing conditions

Air stream temperature—400° F.  
Residence time in air stream—180 seconds

## Molding conditions

Molding die temperature—220° F.  
Platen temperature—320° F.  
Molding pressure—80 p.s.i.  
Molding time—4 seconds

While the gasket was slightly discolored due to inadequate stabilization, the molding step was accomplished satisfactorily.

Coarse resins produced by suspension polymerization have a high surface area and absorb a large volume of plasticizer quite readily. These resins permit a fast processing cycle. A distinct advantage of using such resins in

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sealing compositions of this invention is that processing of the composition is reduced so that the possibility of polymer degradation is minimized considerably.

I claim:

1. A sealing composition consisting essentially of a vinyl chloride resin, having a particle size ranging between about 20 and 200 microns, between about 20 and 250 parts by weight of a plasticizer per 100 parts of resin, between about 0.03 and 10 parts by weight per 100 parts by weight of resin of a thickening agent selected from the group consisting of alkali metal salts of carboxy methyl cellulose, methyl cellulose, hydroxymethyl cellulose, hydroxypropyl cellulose, and mixtures thereof, and ethylene oxide polymers, and between about 30 and 600 parts by weight of water per 100 parts by weight of resin, said composition being immobile at room temperature.

2. A composition according to claim 1 wherein the thickening agent is hydroxyl propyl cellulose.

3. A composition according to claim 2 wherein the resin is polyvinyl chloride.

4. A composition according to claim 1 wherein the viscosity ranges between about 500 and 40,000 centipoises.

5. A composition according to claim 1 which includes a thermally-decomposable solid chemical blowing agent.

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WILLIAM SHORT, Primary Examiner

EARL A. NIELSEN, Assistant Examiner

U.S. Cl. X.R.

260—23, 29.6, 30.6, 31.8; 264—268

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**United States Patent** [19]

Smith et al.

[11] **3,834,578**[45] **Sept. 10, 1974**[54] **FLOWED-IN POLYURETHANE GASKETS  
FOR PAIL AND DRUM COVERS**[75] Inventors: **David B. Smith**, Watertown; **Joel A. Gribens**, Framingham, both of Mass.[73] Assignee: **W. R. Grace & Co.**, Cambridge, Mass.[22] Filed: **June 22, 1972**[21] Appl. No.: **265,148**[52] **U.S. Cl.** ..... **220/46 R**, 215/40, 260/2.5 AK,  
260/2.5 AM, 260/2.5 BE, 260/77.5 AM.[51] **Int. Cl.**... **B65d 53/06**, C08g 22/48, C08g 41/04[58] **Field of Search** ..... 260/2.5 BE, 2.5 AM, 859,  
260/77.5 AM; 220/46 R; 215/40[56] **References Cited****UNITED STATES PATENTS**3,273,743 9/1966 McColl ..... 220/46 R  
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*Primary Examiner*—Donald E. Czaja*Assistant Examiner*—C. Warren Ivy*Attorney, Agent, or Firm*—Armand McMillan; C. E. Parker

[57]

**ABSTRACT**

Superior sealing performance can be imparted to pail and drum covers by equipping them with flowed-in gaskets made from a composition comprising a nitrile rubber, a polyurethane prepolymer and a carbon dioxide blocked polyamine curing agent.

**1 Claim, No Drawings**

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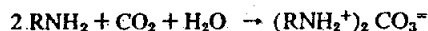
# FLOWED-IN POLYURETHANE GASKETS FOR PAIL AND DRUM COVERS

## THE PRIOR ART

The manufacture of gasketed or sealed closure members for containers, such as metal pail covers and metal drum covers, generally involves, on a practical basis, machinery capable of placing annular layers of sealing compound upon the closure members at a high rate of speed. Once this has been done, the closure member with its liquid gasket is subjected to an appropriate heat treatment, or to moisture as the case may be, to effect the cure of the composition to the desired extent.

For these reasons, the provision of fast-curing sealing compounds to the container closure industry is highly desirable. Yet, keeping in mind the exacting requirements of a good compound for high speed application, none of the known polymeric materials stands out a priori for selection in terms of storage stability, one-package convenience, appropriate low shear and high shear viscosity for ease of application, quick controlled cure and satisfactory gasket properties.

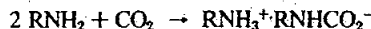
Polyurethanes, for example, provide a good illustration of the expectations of the man skilled in the art with respect to the use presently contemplated. Thus, although polyurethane elastomers have found wide use because of their excellent properties, there exists a problem in the matter of curing agents. Most typically used for this purpose are polyols, water and polyamines. With polyols or water, the cure is relatively slow and, even with heat, no obvious advantage is obtained over the rubber compositions of the art. Furthermore the shelf life of these prepolymers is seriously shortened in the presence of these curing agents. When polyamines are selected as curing agents, on the other had, the reaction is either so fast as to be of no practical significance, as in the case of the lower diamines, or in any event serious problems of stability are encountered which preclude the use of one-package compositions due to the short shelf life of fully compounded materials. As to the use of masked, or blocked polyamines, it has been found (U.S. Pat. No. 3,513,125) that the cure proceeds rather slowly after the initiation of crosslinking, not to mention the undesirability of released acidic blocking agents in a metal-container medium. Part of these potential difficulties may, of course, be avoided by the use of polyamine carbonates as blowing agents. In such compounds the acid moiety is an asset rather than a detriment. But the carbonates, which are formed with carbon dioxide in the presence of water.



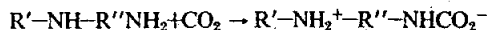
are difficult to use because, when compounded with polyurethane prepolymers, they require relatively long heating periods at elevated temperatures in order to cure. Thus, a one-mil thick layer of castor oil-toluene diisocyanate prepolymer mix with the carbonate of triethylenediamine requires a cure of 30 minutes at 302°F (U.S. Pat. No. 3,425,964). The projection of these parameters to gaskets with thicknesses of twenty mils or more is certainly not very encouraging. Neither, for that matter, is the alternative of substituting for the carbonates their conventional equivalents, the polyamine carbamates. Yet, this is what applicants have done, and with unexpected success if one considers that all the shortcomings of the carbonates can be attributed a priori to the carbamates.

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The blocked curing agents that applicant has found essential for the process of this invention are well known to the art and their preparation is fully described in various publications, including U.S. Pat. Nos. 3,029,227 and 3,344,175. They are prepared in a manner similar to the carbonates with the exception that water is excluded from the reaction mixture:



For a diamine, the reaction becomes:



The product is a stable "inner salt" which can be dispersed in well known fluid isocyanate-terminated polyalkylene ether or polyester prepolymers to form remarkably stable gasket-lining compounds ready for application to closure members without further handling. Once applied and heated for a short time, the carbamate decomposes into the original polyamine and carbon dioxide. The liberated polyamine reacts with the isocyanate groups of the prepolymer to form urea linkages, while the released carbon dioxide serves as a foaming agent. The overall process is quite rapid.

## SUMMARY OF THE INVENTION

It has now been discovered that flowed-in gaskets can be lined on pail and drum covers from a composition comprising a nitrile rubber, a polyurethane prepolymer and a carbon dioxide-blocked polyamine, to yield, after quick curing, gaskets with outstanding sealing qualities and excellent recovery after dry compression.

## DETAILED DESCRIPTION

The compositions of this invention consist essentially of a mixture of low molecular weight polyurethane prepolymer with a nitrile rubber and a finely dispersed polyamine carbamate. Fillers, solvents, antioxidants, pigments and other additives may be incorporated for their conventional effects.

The polyurethane prepolymers usable in this invention are low molecular weight reaction products of polyisocyanates, preferably aromatic, with polyfunctional organic compounds containing active hydrogen. Polyhydroxy compounds are preferred, the best results having been obtained with mixtures of triols and diols in which the ratio of triol hydroxyl groups to the total number of hydroxyl groups in the prepolymer is in the vicinity of about 0.04.

The nitrile rubber used in the present compositions preferably has a "high acrylonitrile" content, i.e., about 38 to 42 percent. Other acrylonitrilebutadiene rubbers may also be used, but with attendant changes in the properties of the final gaskets. The composition of the invention should contain between 10 and 30 percent by weight of nitrile rubber, based on the polyurethane prepolymer content.

The carbamates to be employed with the prepolymers already enumerated are, as already mentioned, the reaction products of polyamines and carbon dioxide under anhydrous conditions. The compounds so prepared are generally stable solid materials which may be pulverized for dispersion into the polyurethane prepolymer or dispersed in an organic non-aqueous inert solvent prior to admixture with said prepolymer. The preferred particle size of the carbamate for mechanical stability of the prepolymer mix and the uniformity of the cured polyurethane mass is such that the powder

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should pass through a 200 mesh or finer U.S. Bureau of Standards screen. Typical examples of usable carbamates are provided in U.S. Pat. Nos. 3,029,227 and 3,344,175.

The polyamines that are useful in the formation of the protected curing agent are those di-, tri-, tetra-, and other polyamines having at least one active hydrogen atom for each amine group in order that the amine group be capable of combining with carbon dioxide to form the carbamate. The presence of active hydrogen atoms is necessary for the subsequent reaction with the prepolymer. The polyamines having primary and secondary groups readily combine at about room temperature (72°F) with carbon dioxide.

The preferred amines are those compounds containing terminal amino groups. Illustrative species are: 1,2-butanediamine; propylenediamine; 1,3-propane diamine; N,N'-dimethyl-1,3-propane diamine; N,N'-diethyl-1,3-propanediamine; 1,4-butanediamine; 1,6-hexanediamine; ethylene diamine; N-allylethylenediamine; cadaverine; putrescine; pentaethylenhexamine; hexaethylenheptamine and heptaethylenoctamine. Other useful polyamines are 3,8-diaza-1,10-decanediamine; triethylenetetramine; 1,4-bis(1,3-diaminopropyl)-n-butane; 1,3,5,7-heptanetetramine; tetraethylenepentamine; diethylenetriamine; 3,3'-diamino-dipropylamine; and 1,3,6-hexanetriamine.

Subject to the preferences already expressed in terms of prepolymers, i.e., partial reaction products of aromatic diisocyanates with mixtures of diols and triols, such as polyalkylene glycols, and polyhydroxy polyethers, such as polypropylene oxide adducts of hexane triol, there may be used other polyisocyanates and polyhydroxy compounds to achieve useful, if not optimum properties in the gaskets.

Among the polyisocyanates that may be employed in this manner are: the various unsubstituted phenylene diisocyanates, as well as those having one or more substituents such as methyl and other lower alkyl groups having up to about 4 carbon atoms, halogen atoms, nitro groups, alkoxy and aryloxy groups; various substituted and unsubstituted biphenylene diisocyanates; substituted and unsubstituted diphenyl diisocyanates such as the diphenylmethanes-, the diphenylisopropylidenes- and the diphenylsulfone diisocyanates; the naphthalene diisocyanates; alkylene diisocyanates containing up to about 10 alkylene carbon atoms; cycloalkyl diisocyanates containing one or more cycloalkane rings such as 1,3-cyclopentene- and 4,4'-dicyclohexylmethane diisocyanate; and other diisocyanates such as 1-ethylenedisocyanato-4-phenylisocyanate. Examples of tri- and tetra- isocyanates that may be used include the benzene and toluene trisocyanates, 2-methyl-2-(4-isocyanatophenyl)-trimethylene diisocyanate, tetrakis(4-isocyanatophenyl)methane and bis-(4-methyl-2,5-isocyanatophenyl)methane. Polymeric materials such as polymethylene polyphenylisocyanate may also be employed.

Suitable compounds that will react with the above isocyanates to yield the necessary prepolymers include polyols such as ethylene glycol, glycerol, pentaerythritol, sorbitol, triethanolamine, as well as polymeric compounds such as polyglycols, polyhydroxy polyesters, polyhydroxy polyesteramides and polyhydroxy polyether oils.

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Typical polyglycols include polyalkylene glycols, such as polyethylene glycol, polypropylene glycol, and polybutylene glycol.

Representative polyesters are reaction products of dihydric alcohols, such as ethylene glycol, diethylene glycol, tetraethylene glycol, 1,3-propylene glycol, dipropylene glycol, or higher polyhydric alcohols such as glycerol, trimethylol propane, pentaerythritol, mannitol, or mixtures of two or more of the alcohols with a polycarboxylic acid or anhydride such as succinic, adipic, glutaric, malonic, sebacic, azelaic, phthalic, terephthalic, isophthalic, trimellitic and pyromellitic acids and their anhydrides. Mixtures of the acids and anhydrides can be employed.

Illustrative polyhydroxyl polyesteramides are the reaction products of a polyhydric alcohol with a dicarboxylic acid, examples of both of which have been mentioned above, and as necessary, diamines or aminoalcohols such as ethylene diamine, hexamethylene diamine, phenylene diamine, benzidine and monoethanolamine.

Examples of polyhydroxy polyethers include linear hydroxyl-containing polymers and copolymers of cyclic ethers such as ethylene oxide, epichlorohydrin, 1,2-propylene oxide, oxacyclobutane, and tetrahydrofuran, or branched polyethers obtained from the condensation of the aforementioned ethers with branched polyhydroxy compounds such as glycerol, 1,1-trimethylolpropane, pentaerythritol, sorbitol and sucrose. Mixtures of linear and branched polyethers or mixtures of polyesters and polyethers can also be employed.

Other polyhydroxyl materials, for example, esters of hydroxycarboxylic acids, such as castor oil and glyceryl monoricinoleate, can also be used.

The solid polyurethane polyurea which results from the curing of the sealing compositions of interest may be crosslinked to any degree desired, depending on the number of functional groups present and the ratio of amino groups to isocyanate groups.

Satisfactory crosslinking of the polymers used in this invention is generally achieved with terminal isocyanate group to carbamate chemical equivalent ratios within the range of 1.15:1 to 1:1.30. These proportions may also vary more broadly depending on the particular nature of the components used and the degree of crosslinking required by the application intended for resulting polymer.

The temperature at which the polyurethane foam is formed depends upon the nature of the prepolymer used and the decomposition temperature of the carbamate. Although a temperature of about 150°F can be used, the range of 200°F to 300°F is generally preferred. At 300°F, for instance, most compositions foam to a uniform cell structure in as little as 2 minutes for a foam thickness of about 0.25 inches.

The compositions of the invention will generally contain a solvent to facilitate handling of the prepolymer mix by gasket-laying machinery. Such solvents are organic liquids that do not possess any active hydrogen to react with the isocyanate groups of the polymer and are capable of evaporating under process conditions. Examples of suitable liquids for this purpose include: aromatic hydrocarbons, such as benzene, toluene and xylene; acetic esters, such as ethyl and butyl acetates; chlorinated aromatic and aliphatic solvents, such as monochlorobenzene and carbon tetrachloride; ethers,

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such as butyl ethyl ether, dioxane and hydrofuran; and ethylene glycol monomethyl ether acetate. Solvents having active hydrogen such as the lower alcohols, may be used to prepare the carbamate, if that is done, but they must be removed from the dispersion before it is mixed with the prepolymer.

Conventional plasticizers may also be incorporated into the compositions used in the practice of the invention, the preferred materials being phthlate esters. Examples of these materials, which may be used with or in lieu of a solvent, are dioctyl phthalate, diisodecyl phthalate and the like.

As fillers, when such are desired, there may be used, for example, calcium carbonate, calcium silicate, aluminum silicate, silica, chrysolite asbestos, carbon black, titanium dioxide, fully calcined clays and talcum powder.

The following examples are provided to illustrate the invention. All parts and percentages therein are on a weight basis, unless otherwise specified.

#### EXAMPLE 1

A polyurethane-nitrile rubber gasket composition is prepared from the following ingredients:

Material	Parts by Weight
Polyoxypropylene glycol, M.W. 2000 average	28.18
Hexanetriol, polypropylene oxide adduct, M.W. 2500 average	3.31
Diethylene glycol	1.66
Nitrile rubber, 40% acrylonitrile	10.44
Calcium carbonate	27.85
Benzoyl chloride	0.51
Toluene diisocyanate	14.80
CO <sub>2</sub> -blocked diethylene triamine	4.46
Toluene	5.60
Sodium bis-(tridecyl)sulfosuccinate	0.68
Hydrogenated castor oil	0.11
Organo-silicon copolymer surfactant	2.38

The three hydroxyl group-containing compounds were mixed together and heated at 190°F for 2 hours while stirring in vacuo. The dried mixture was cooled to 80°F. The nitrile rubber, calcium carbonate and benzoyl chloride were then thoroughly dispersed into this mixture. The diisocyanate was added and the resulting mixture heated to 170°F and maintained within 167°F to 176°F for 1.5 hours. A prepolymer was thus obtained having a —NCO titer of about 5 percent, and a triol to total hydroxyl group ratio of about 0.04.

A suspension was prepared with a pulverized carbamate resulting from the treatment of diethylene triamine with carbon dioxide under anhydrous conditions. The last three ingredients, i.e., surfactants and foam stabilizers, were added to the toluene and the carbamate was mixed in. The resulting dispersion was

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added to the prepolymer-rubber mixture to yield the final stable, curable preparation. The organo-silicon copolymer used is a copolymer of dimethylsiloxane, ethylene oxide and propylene oxide.

#### EXAMPLE 2

The gasket-channel of 12-inch metal pail covers were lined by means of automatic lining machinery with an appropriate quantity of gasketing compound. The lining operation was carried out at the rate of about 40 covers per minute per lining station. The lined covers were then passed through an oven where they were allowed to reside long enough to convert the liquid gasketing compositions to fine-celled resilient non-tacky foam. The type of composition, the quantity lined, as well as the heating time and temperature, are listed in the following table.

TABLE I

Type	Lined 12-inch Pail Covers		
	Quantity	Time	Temperature
Polyurethane/NBR (Example I)	9 g	20 minutes	260°F
SBR Cover Compound II	18 g	90 minutes	250°F
SBR Cover Compound III	18 g	90 minutes	250°F

The SBR cover compounds used here for comparison purpose are commercial products widely used in the container industry. These cover compounds contain about 30 percent, dry weight, of a 25:75 styrene-butadiene rubber, 60 percent calcium carbonate, as well as the usual conventional stabilizers, curing agents and surfactants in the proportions required to give them their specific characteristics. SBR Cover Compound II yields a soft deformable cured product while SBR Cover Compound III cures to a harder, less deformable substance.

The pail covers lined in the manner of Example 2 were tested for sealing capacity, resilience of gasket and resistance to various liquids.

In the first type of test, typical liquids were placed in 5-gallon pails, gasketed covers were crimped on, both lacquered and plain, and the loss of liquid on storage by diffusion through the gasket was measured by weighing after various time intervals. One set of pails was weighed at the end of 30 days of storage. These pails were then opened, resealed, and weighed again 7 days later. Another set was weighed after 60 days of storage, opened, resealed and again weighed seven days later. The losses of liquid, in pounds, which took place under these conditions are reported in Table II.

TABLE II

SOLVENT LEAKAGE TEST									
After 30 Days Gasket Compound	Solvent	Loss (lbs)		Loss (lbs) Reclosed for 7 Additional Days		Loss (lbs) After 60 Days		Loss (lbs) Reclosed for 7 Additional Days	
		Plain Cover	Lacquered Cover	Plain Cover	Lacquered Cover	Plain Cover	Lacquered Cover	Plain Cover	Lacquered Cover
Polyurethane - NBR I	ethyl alcohol	0.00	0.00	0.00	0.00	0.00	0.25	0.15	0.12
SBR Compound II	ethyl alcohol	1.31	1.03	0.34	0.25	1.61	0.38	0.47	1.00
SBR Compound III	ethyl alcohol	0.00	1.07	0.81	0.67	0.61	1.50	1.60	0.83
Polyurethane - NBR I	methylethyl ketone	0.00	0.00	0.00	0.00	0.19	0.19	0.15	0.12
SBR Compound II	methylethyl ketone	0.00	0.00	0.00	0.00	0.00	0.12	0.15	0.15
SBR Compound III	methylethyl ketone	0.00	0.00	0.00	0.00	0.12	0.19	0.50	0.12
Polyurethane - NBR I	lacquer thinner	0.00	0.00	0.00	0.00	0.00	0.12	0.00	0.10
SBR Compound II	lacquer thinner	0.00	0.00	0.00	0.00	0.00	0.12	0.15	0.12
SBR Compound III	lacquer thinner	0.00	0.00	0.00	0.00	0.19	0.12	0.12	

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It becomes apparent from the results in Table II that the polyurethane gaskets (I) are superior as sealants for ethyl alcohol type of liquids, while being equal or slightly better than those of the prior art (II and III) with respect to other common organic solvents.

In the second series of tests, the gasketed covers of Example 4 were crimped on metal pails, allowed to remain there under compression for the period and at the temperature indicated. Compression was determined by measuring the thickness of the gasket at the various stages. Recovery was measured in the same manner at the times indicated.

The results of this tests are summarized in the following table.

TABLE III

Gasket Compound	DRY COMPRESSION SET (Percent Recovery)								
	60% Compression at			60% Compression at			40% Compression at		
	R.T. for 30 Days			100°F for 30 Days			R.T. for 30 Days		
	Immediate Recovery	1 Hour Recovery	1 Week Recovery	Immediate Recovery	1 Hour Recovery	1 Week Recovery	Immediate Recovery	1 Hour Recovery	1 Week Recovery
I	91	97	100	90	100	100	85	99	100
II	77	79	86	75	77	85	73	76	90
III	85	89	96	82	84	90	83	88	91

I. Polyurethane - NBR I

II. SBR Cover Compound II

III. SBR Cover Compound III

The quick and superior recovery of polyurethane gaskets (I) is again apparent on comparison with the behavior of conventional gaskets (II and III). The polyurethane gaskets of this invention evidently possess a high degree of resilience.

The resistance of the various gaskets to common liquids was tested by immersing cured gasket material in a given liquid for certain periods of time and determining the loss in weight of said gasket material after complete removal of the liquid. The data of the tests carried out in this manner is summarized in Table IV.

TABLE IV

SOLVENT EXTRACTION				
Gasket Compound		Solvent	% Loss After 2 Weeks	% Loss After 4 Weeks
Polyurethane - NBR	I	Water	2.8	1.4
SBR Compound	II	Water	4.2	5.9
SBR Compound	III	Water	1.5	1.8
	I	Ethyl Alcohol	4.2	7.7
	II	Ethyl Alcohol	11.5	9.5
	III	Ethyl Alcohol	11.8	12.1
	I	Methylethyl Ketone	5.7	6.2
	II	Methylethyl Ketone	11.8	14.1
	III	Methylethyl Ketone	12.1	12.3
	I	Methylene Chloride	4.7	4.4
	II	Methylene Chloride	12.2	11.3
	III	Methylene Chloride	11.7	11.7
	I	Lacquer Thinner	1.4	2.0
	II	Lacquer Thinner	10.4	9.4
	III	Lacquer Thinner	10.6	11.3
	I	Toluene	3.1	3.3
	II	Toluene	9.6	6.8
	III	Toluene	10.7	16.6
	I	Naphtha	0.9	2.0
	II	Naphtha	9.3	9.4
	III	Naphtha	10.9	11.3

Again, the overall superiority of polyurethane gaskets becomes evident.

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In summary, the present invention relates to cover gaskets which not only benefit from the processing ease attending stable one-package fast-curing polyurethanes, but also perform in a superior manner under the type of conditions generally availing in their field of application. Although a number of examples have been provided here to illustrate various operational features of the invention, it is apparent that the man skilled in the art can devise several other embodiments which will be substantially within the scope of the invention as described in the appended claims.

What is claimed is:

1. A cover for a rigid impermeable container,

equipped with a flowed-in cellular resilient peripheral gasket which is the cured product of a composition comprising: (a) a liquid polyurethane prepolymer consisting of a free isocyanate group-containing reaction product of a polyisocyanate compound with a polyhydroxy material substantially composed of polyhydroxy polyether oils; (b) a finely divided polyamine carbamate; and (c) about 10 to 30 percent by weight, based on the polyurethane prepolymer of an acrylonitrile-butadiene rubber having an acrylonitrile content of

about 38 to 42 percent.

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